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REACTOR FUEL PROCESSING

A Quarterly Technical Progress Review

Prepared for DIVISION of TECHNICAL INFORMATION,
U. S. ATOMIC ENERGY COMMISSION, by ARGONNE NATIONAL LABORATORY

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REACTOR FUEL PROCESSING

A REVIEW OF RECENT DEVELOPMENTS

Prepared for DIVISION of TECHNICAL INFORMATION,
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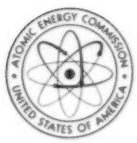

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foreword

This quarterly review of reactor fuel processing has been prepared at the request of the U. S. Atomic Energy Commission, Division of Technical Information. It is intended to assist those interested in keeping abreast of important developments in this field. In each Review it is planned to cover those particular subjects in which significant new results have been obtained. The Review does not purport to abstract all the literature published on this field during the quarter. Instead it is intended to bring each subject up to date from time to time as circumstances warrant.

Interpretation of results, where given, represents the opinion of the editors of the Review, who are personnel of the Argonne National Laboratory, Chemical Engineering Division. Those taking part in the preparation of this issue are J. Barghusen, L. Burris, Jr., I. G. Dillon, P. Fineman, J. Fischer, A. A. Jonke, S. Lawroski, W. J. Mecham, D. Paige, J. Royal, W. B. Seefeldt, R. K. Steunenberg, C. E. Stevenson, and R. C. Vogel. The reader is urged to consult the original references for more complete information on the subject reported and for the interpretation of results by the original authors.

The second edition of the *Reactor Handbook*, Vol. II, *Fuel Reprocessing*, has been published in a completely revised and enlarged form. The volume, which was prepared under contract with the USAEC, is edited by S. M. Stoller and R. B. Richards. The objective of this edition is to present a condensed version of the staggering amount of data which has accumulated in the reprocessing field. The data are organized along patterns of functional usage (similar to the organization of this Review) and places emphasis on author references and correlating data rather than mere compilation. The editors believe that the book is essentially current as of early 1960. Since this volume represents an important major source of information in the field, the subject headings of each chapter are listed as an appendix to this issue.

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Section 1

COMMERCIAL ASPECTS OF FUEL PROCESSING

Fuel-Cycle Costs

The AEC Office of Operations Analysis and Forecasting has issued a report on costs of nuclear power from stationary plants designed primarily for the generation of electricity.[1] One section of the report deals with the costs of the fuel cycle, including fabrication of fuel elements, transportation of irradiated elements, chemical processing, chemical conversion of recovered special nuclear materials, the use charge for leased fuel, the charge for fuel consumption, and the credit for plutonium and U^{233} produced. The following discussions contain some of this information.

Transporting Irradiated Fuel Elements

The cost of transporting irradiated fuel elements in the United States from a reactor site to a chemical processing plant has been estimated, in the table below, for slightly enriched fuel and for distances of about 3000 miles. It was assumed that the cooling time prior to shipment is 120 days or more, that all shipments comply with the federal regulations, that adequate property insurance coverage is provided, that couriers are not required, and that casks are available on a rental basis. Estimates were made for two cask sizes: a 30-ton cask carrying 2000 lb of uranium, and a 70-ton cask carrying 7600 lb of uranium. As shown in the following table, the largest cask has an economic advantage where requirements of nuclear safety and heat dissipation can be satisfied. The factors that contribute most to the uncertainties in these costs are the insurance rates, the choice of cask size and weight, cooling time prior to shipment, and effect of negotiations on carrier rates.[1]

	Transportation costs, dollars per kg of uranium	
	30-ton cask	70-ton cask
Freight from reactor to processing plant	2.40	1.50
Freight for return of empty casks	2.30	1.40
Cask rental	2.90	2.00
Property insurance	1.50–6.00	1.50–6.00
Total	9.10–13.60	6.40–10.90

Since a number of reactors will soon be ready for refueling and since construction of both foreign and domestic reactors is steadily increasing, there is a need for irradiated fuel-element cask designs and shipping procedures which will be acceptable from the radiological and criticality standpoints. In March 1960 AEC published for public comment a proposed regulation to guard against accidental criticality, radiation exposure to individuals, and the release of fission products during the shipment of spent fuel elements from reactors to processing plants. In May 1960 a conference was held by AEC to obtain the views of a group of industrial concerns and government agencies concerning such shipments. Problems in the design and shipment of such casks include containment of radiation intensity as high as several thousand roentgens per hour at the surface of the fuel elements, high heat output resulting from radioactive decay, and the need for structural integrity under all conditions of shipment and under severe impact.[2]

Chemical Processing and Conversion Costs

The AEC charges for chemical processing of irradiated fuel were first announced in March 1957 and were discussed in a previous issue of

this Review.[3] AEC charges are obtained by multiplying a fixed daily charge times the number of days required to process a given batch of fuel, including the time for startup, shutdown, and cleanup of the processing facilities (turn-around time). Owing to escalation, the daily charge has risen from $15,300 in March 1957 to $17,000 computed[1] as of August 1960. The number of processing days required depends on the processing rate for the hypothetical plant on which the charges are based. This processing rate depends on the U^{235} assay of the unirradiated fuel, ranging from 1000 kg of uranium per day for U^{235} assay of 3 per cent or less to 44 kg per day for 93 per cent U^{235}.

The turn-around time needed is assumed to be not less than two days nor more than eight days and otherwise equal to the number of processing days for a given batch of fuel. The portion of the total fuel-processing charge that is for turn-around time tends to be higher for the smaller reactors because of the lesser amounts of uranium involved. In some cases this charge can be reduced by holding fuel elements to accumulate a larger batch. However, such a cost reduction needs to be weighed against increases in use and storage charges and increases in working capital resulting from delayed credit for plutonium.[1]

Chemical processing plants usually yield purified solutions of uranium nitrate and of plutonium nitrate, whereas the form to which AEC credits apply is the hexafluoride for uranium and the metal for plutonium. The AEC charge for converting uranium nitrate to hexafluoride is currently $5.60 per kilogram of uranium (for U^{235} assays of 5 per cent or less), and the charge for converting plutonium nitrate to metal is $1.50 per gram of plutonium.

There will be some irrecoverable losses of uranium and plutonium in each step of processing and conversion. For AEC chemical processing services, the losses are assumed to be 1 per cent of the value of the uranium and plutonium delivered to the processing plant. Losses for the conversion to final products have been announced in a recent AEC news release.[4] These are 0.3 per cent of the amount of uranyl nitrate to be converted to hexafluoride and 1 per cent of the amount of plutonium nitrate to be converted into metal. Total losses for processing and conversion are therefore 1.3 per cent of the uranium and 2 per cent of the plutonium.

Two examples of processing and conversion charges are given below.

	Estimated charges, dollars per kg of uranium	
	Yankee type reactor	Piqua type reactor
Chemical processing time	17.50	17.00
Turn-around time	6.60	17.00
Conversion to UF_6	5.60	5.60
Conversion to Pu metal	7.40	4.10
Loss of uranium	4.20	2.10
Loss of plutonium	1.20	0.60
Total	42.50	46.40

The Yankee reactor fuel is stainless-steel-clad uranium oxide (3.4 per cent U^{235}), and the Piqua reactor fuel is aluminum-clad uranium-molybdenum-aluminum alloy (1.94 per cent U^{235}). It is assumed that the batch for chemical processing consists of one reactor core. Similar estimates for other slightly enriched reactors like Dresden, Hallam, Carolinas-Virginia, Florida, and BONUS give total processing and conversion charges ranging from about $34 to $50 per kilogram of uranium.[1]

In the case of highly enriched fuels of uranium-aluminum alloy of the type normally used in research and test reactors, the AEC charge for chemical processing is based on a daily processing rate of 400 kg of uranium plus aluminum, including end boxes. AEC has recently established a new charge for fuel of this type where the processing batch contains less than 400 kg. This charge is $145 per kilogram of the total weight of uranium and aluminum, provided that the U^{235} content does not exceed 10 per cent of the total weight of uranium and aluminum metal. Charges for conversion, losses of material, and use charges also apply to such fuels.[4]

Use Charges and Fuel Consumption Charges

Domestically, AEC does not sell enriched uranium but leases it, assessing an annual use charge as a percentage of the value of the material. The fuel inventory for a nuclear plant includes material that is in storage at the reactor site, under irradiation in the reactor, being cooled after discharge, in shipment to and storage at the chemical processing site, and undergoing chemical recovery and conversion. The utility pays AEC every six months for

the accumulated use charge and for uranium that has been consumed by burnup or loss. The burnup cost is the difference between the charge for the uranium in fresh fuel and the credit for uranium in spent fuel.

On July 1, 1961, AEC reduced its base charges (schedule of values) for enriched and depleted uranium and increased its use-charge rate.[5] The reduction in base charges varies from 20 per cent for highly enriched uranium to 34 per cent for uranium containing 1 per cent U^{235} and ranging to 63 per cent for depleted uranium. The new charges are published in the *Federal Register* for May 30, 1961. As an example, the charge for uranium (as the hexafluoride) containing 2 per cent U^{235} is $160 per kilogram of contained uranium or $8 per gram of contained U^{235}. The previous charge had been $11 per gram of contained U^{235}. The reduction is made possible by decreased costs of natural uranium.

The use-charge rate was increased from 4 to 4.75 per cent. The new rate takes account of the increased cost of money to the U. S. Government. For most licensed reactors in the United States, the use charge for enriched uranium is waived during the first five years of operation. The net effect of the changes in use charges and base charges will be to lower the cost of nuclear power—the reduction varying from one reactor to another.

The revision of the schedule of charges for enriched and depleted uranium does not affect the prices that AEC will pay for plutonium and U^{233} produced in reactors through June 30, 1963. These prices take into account the weapon value. There are no AEC commitments for prices to be paid for these materials after that date. If the estimated fuel (nonweapon) values of plutonium and U^{233} were related to the revised charges for enriched uranium, they would be reduced by about 20 per cent. The fuel values would decrease from $12 to about $9.50 per gram of plutonium as metal and from $15 to $12 per gram of U^{233} as nitrate. These are calculated as energy values, based on the relative heat release per fissionable nucleus consumed, and do not take into account the relative costs of fabricating or processing the various fuels or the amounts of new fuel generated during irradiation. The former tends to decrease and the latter to increase the fuel values[5] of plutonium and U^{233}.

Fuel-Processing Plans

The AEC is now planning to use only the Savannah River Plant and the Idaho Chemical Processing Plant (ICPP) for all processing services for U. S. and foreign nonproduction reactors. Previously it had been intended to distribute the load among four sites, Savannah River, Idaho, Hanford, and Oak Ridge. Idaho will receive all fuels with U^{235} isotopic concentrations above 20 per cent, and Savannah River will get low-enrichment fuels.[6]

In June 1961 AEC signed its first contract making financial arrangements for the processing of irradiated fuels from a licensed reactor. Fuel elements used in the original core of the Vallecitos Boiling Water Reactor (VBWR) will be accepted at the Idaho site. The AEC might not process the used fuel elements immediately.[7]

The AEC has offered processing services until June 30, 1967, or until private processing at reasonable cost is available. The AEC still hopes to see private capacity for chemical processing installed, particularly with reference to the processing of private reactor fuels. However, it now appears that it will be one or two years before the most actively interested group [the Industrial Reprocessing Group (IRG)] plans to reach a firm decision to proceed. During this period the IRG will conduct a more detailed study to cover shipping problems, licensing, legal and accounting questions, fuel storage, and more detailed economics. The new study will be sponsored by the original IRG members, possibly joined by other utilities, and will be conducted by Davison Chemical Division with three subcontractors.[8] The AEC has meanwhile deferred the processing of such power-reactor fuels in AEC facilities and is constructing facilities at Savannah River to receive and store irradiated fuels for processing at a later time.[9]

Preliminary plans for the Eurochemic processing plant have been completed. Construction work was scheduled to begin in the fall of 1961. Plant capacity has been set at 350 kg of natural uranium per day and 200 to 250 kg of uranium per day enriched to 5 per cent. Acceptable fuels are uranium-aluminum, uranium-molybdenum, or uranium dioxide clad in aluminum, magnesium, zirconium, Zircaloy, or stainless steel. Plans include storage facilities for 80 tons of fuel awaiting processing. The plant will have two fuel dissolvers: one for enrichments to 1.6

per cent and the other for higher enrichments. The process is a two-cycle solvent-extraction type using tributyl phosphate in hydrocarbon diluent. Construction is now scheduled for completion in July 1963, and the first active runs[6] should begin by July 1964.

The AEC has recently amended its regulations to eliminate a requirement that a "production-facility" license be obtained for the processing of slightly irradiated uranium. Some irradiated materials may contain such small amounts of fission products and such low levels of activity that no additional radiological safety precautions are required beyond those necessary for the processing of unirradiated materials. The processing of such low-level irradiated materials can now be treated similarly to unirradiated materials from a licensing standpoint. The specified limits for concentrations and quantities of induced radioactivity are very low. However, the amendment would have the effect of exempting from the production-facility license requirement the processing of many fuel elements used in critical facilities, if the elements are cooled for an appropriate period of time prior to processing. The amendment will apply to the proposed recovery, by Engelhard Industries, Inc., Newark, N. J., of the 20 per cent enriched uranium contained in fuel and control elements from a Netherlands research reactor. The actual operating time with the elements in place amounted to only about a week.[10]

Waste Disposal and Fission-Product Recovery

The first commercial land-burial site for radioactive waste (low level) is to be operated by Nuclear Engineering Company of Pleasanton, Calif., on an 80-acre site located about 100 miles northwest of Las Vegas, Nev. Lease arrangements with the State of Nevada are expected to be completed soon. The Company has applied for an AEC license for storing radioactive waste aboveground at that location and has indicated that it will file for a license for waste burials in the near future. The Company also expects to build a decontamination and repair facility at the site.[11]

The State of New York is planning to set up a nuclear service center for temporary and long-term storage of nuclear fuels, by-products, and wastes at a site about 35 miles south of Buffalo. The 3500-acre site will also be available for related industrial development, particularly fuel processing. The center will be owned by the State, and storage operations will be conducted by an industrial company under contract to the State Office of Atomic Development. Twenty-five industrial firms have expressed interest in becoming the contractor. The center is scheduled to be opened for low-level-waste storage[12] by the spring or summer of 1962.

The AEC has announced that it is setting up facilities at Hanford to separate fission products from production-plant waste streams in refined, chemical form in megacurie quantities beginning about mid-1963. The isolated fission-product compounds will be made available to industry for final processing and fabricating into "nuclear batteries" and other devices. Of principal interest are Sr^{90}, Cs^{137}, and Ce^{144}, although the Hanford facilities will also be able to separate Pm^{147}. The AEC considered inviting private industry to undertake the recovery operation. However, indications are that at present it would be more feasible for AEC to recover the fission products and offer them for sale to industry. The assured availability of these materials at reasonable prices should foster development and use of the materials.[13]

In April a successful cross-country shipment of 120,000 curies of Cs^{137} and 20,000 curies of Sr^{90} was made from Hanford to Oak Ridge. At Oak Ridge the strontium is being processed for delivery in titanate form to the Martin Company for loading into a 5-watt remote weather station for the U. S. Weather Bureau.[14]

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Section II

RESEARCH AND DEVELOPMENT ON AQUEOUS PROCESSING

Processes for separating valuable products from used reactor fuels and for making them available for reuse may be grouped as being generally of aqueous or nonaqueous types. The aqueous processes for the most part involve preparing ionic solutions of uranium or plutonium by one means or another, upon which the separating operation (i.e., extraction, precipitation, and sorption) is conducted. The aqueous processes have many features in common, have been extensively developed, and are largely distinct in function and technology from the nonaqueous processes. Advances are reviewed as they affect means of fuel preparation; the separating techniques of extraction, precipitation, and ion exchange; the equipment, instruments, and plant operating experience; the special technology of homogeneous reactor fuels; and the problems encountered in corrosion of materials of plant construction.

Preparation for Fuel Processing

Aqueous separation processes were first developed for recovering plutonium from production-reactor fuels and then were devised to permit recovering the unused uranium fuel as well. Fuel preparation simply involved dissolving fuel cans in caustic and uranium slugs in nitric acid. Power-reactor fuels are generally much more complex than the aluminum-clad uranium used for plutonium production elements, with regard to both structure and materials. Consequently, a variety of reagents and processes are required to dissolve the cladding and alloying elements, and for some fuels advantages result from mechanical disintegration or jacket removal.

Mechanical Processing by Shearing

Inasmuch as many of the claddings of nuclear fuels are chemically resistant, it is often desirable to remove the cladding material mechanically. The important advantages of mechanical processing include production of smaller aqueous waste volumes, use of less corrosive reagents for dissolving the fuel material after the cladding is removed, and possible increased plant capacity in the absence of the dissolved cladding material in the process streams. However, new problems are generated by this process, and these include the design and maintenance of shears and saws and the confinement of radioactive fines generated by cutting.

Hanford reports in detail on the problem of confinement of radioactive fines in connection with work being done on the "mechanical cell."[1] Work was done on cold simulated fuel elements chopped under water using the 40-ton hydraulic shear.

The system tested consisted of a horizontal fuel-element feed trough connected at a right angle to the cylindrical throat of the shear. Under the shear discharge chute, the dissolver canister was placed and held tightly to form a seal and to catch the sheared material (see Fig. II-1). A water level was maintained in the trough and throat by the continuous recycling of the water leaking from the shear-assembly-canister seal. The shearing complex described above shows promise as a method for the preparation and loading of dissolver feed material for core-leaching operations. All components of the system can be made geometrically safe for the handling of uranium fuels containing up to 5 per cent U^{235}. The auxiliaries (5 gal/min

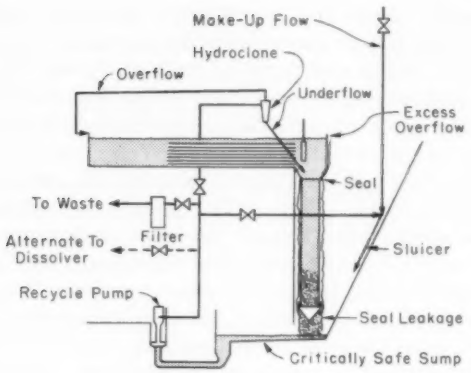

Fig. II-1 Fuel shearing system for fines collection.[1]

pump, $1\frac{1}{2}$-in. hydroclone, and disposable felt filter cartridge), used for the accumulation and confinement of the dispersed uranium dioxide fines in the water, were found to be effective, inexpensive, and easy to operate. Essentially all the material sheared in a 5-ton batch of fuel (campaign) can be loaded into the dissolver canisters for transport to a core-leach dissolver. By continuously recycling all leakage in the system, the uranium dioxide fines produced in the shearing operation can be kept in suspension and continuously loaded out with each dissolver canister. At the completion of the shearing campaign, the small quantity of fines remaining in the recirculation water is filtered through a disposable cartridge filter to recover the remaining uranium dioxide. The cartridge is then placed in the most recently filled dissolver canister. The leakage rate of the shear-canister seal in the shear prototype tested was less than the capacity of the hydroclone (< 2.5 gal/min). The hydroclone efficiency during shearing of thermally cycled sintered uranium dioxide fuel rods, while recycling, was > 90 per cent on the fine uranium dioxide dispersion fed to it.

Essentially 100 per cent removal of the uranium dioxide in suspension at the completion of shearing swaged uranium dioxide material (worst case) was accomplished by passing the slurry through a 5-μ rated felt filter cartridge. The filter material and filter recommended for final bath cleanup is a mechanically interlocked Arnel felt (20-μ-diameter fibers) made into a stacked disk type cartridge, wherein the density of the felt is 40 per cent of its theoretical density. The minimum filter area is estimated as 5 sq ft. This can be easily attained in a cylinder 6 in. in diameter and 12 in. high. Such a filter should handle up to 20 lb of uranium dioxide fines (estimated amount expected in the slurry upon completion of a 5-ton shearing campaign). The Arnel felt completely dissolves in 4M nitric acid, and laboratory batch solvent-extraction tests on typical feed solution show no adverse effects of this material on the Redox process.

A method has been developed at Hanford for the safe deactivation of the sodium-potassium alloy (NaK) reservoirs present in the ends of the stainless-steel-clad uranium or uranium-molybdenum alloy core type fuels.[1] The NaK reservoirs are cut open by hack sawing them at a controlled rate under a submerged hood in a shallow water bath. Since the NaK-water reaction is vigorous, the cutting rate is regulated so that the NaK exposure rate does not exceed the off-gas handling capacity of the submerged hood. Hydrogen (from the reaction of NaK with water) explosions are prevented by diluting the hydrogen emerging from the submerged hood with air to the lower explosive limit. A high-efficiency wet scrubber (Peabody scrubber) was used for the off-gas removal of the fumes from the NaK-water reaction.

Chemical Removal of Stainless Steel and Similar Jacket Metals

Dejacketing with Sulfuric Acid. A batch process has been described for removing stainless-steel cladding from uranium dioxide pellet fuel by dissolving in 4M sulfuric acid; uranium dioxide is subsequently dissolved in nitric acid.[2] Since criticality limitations for enriched fuels require the use of safe vessels, Oak Ridge National Laboratory (ORNL) has studied dejacketing such fuels semicontinuously in a 4-in.-diameter tall pipe dissolver.[3] The dejacketing reagent was continuously supplied to and withdrawn from the dissolver, which contained a single charge of simulated fuel. Dissolution of thin (20 to 38 mils) type 304L stainless-steel plates and tubing in boiling 4M or 6M sulfuric acid was undertaken. Some of the tubing was in the form of prototype Consolidated Edison reactor fuel assemblies, containing uranium dioxide–thorium dioxide pellets. Reaction rates ranged from 1 to 3 mg/(cm^2)(min) based on initial cladding area. Dissolution proceeded satisfactorily but somewhat irregularly, but bumping and foaming were not

excessive. In the processing of plates, the metal content of the dissolver effluent typically decreased from about 90 to 30 g/liter during the course of a dissolution. Tubing, even from a single source, dissolved more slowly (3 to 4 hr for 20-mil material) and less regularly than plates, and some unattacked material remained after the bulk had dissolved. From the simulated Consolidated Edison fuel, losses of uranium and thorium did not exceed 0.2 per cent. The dissolver effluent passed through two settling chambers and into a centrifuge. Suspended solids (chiefly alloy particles) were removed by these means. In other work on this process at ORNL, Gens has shown that exposure to air during the decladding operation slowly increases the losses of uranium and thorium to the decladding solution (to as high as 0.6 per cent uranium loss in 30 hr with fresh 6*M* sulfuric acid), and irradiation also causes slight increases in uranium and thorium losses.[5]

Dejacketing with Nitric-Hydrochloric Acid Mixtures. Stainless-steel cladding materials may also be dissolved in mixtures of nitric and hydrochloric acids which are of the aqua regia type. Such procedures are applications of the Darex processes. In studies of dissolving simulated Consolidated Edison fuel-element tubes (type 304L stainless steel) in 5*M* nitric acid–2*M* hydrochloric acid, Gens[5] found that, as also occurs with sulfuric acid decladding, uranium and thorium losses increase with irradiation and exposure to air. With nitric-hydrochloric acid, the effect is greater with reagents containing 60 g of dissolved stainless steel per liter than with fresh mixed acids. Gens has also studied the generation of hydrogen and nitrous oxide in dissolving stainless steel in nitric-hydrochloric acid mixtures.[6] The principal off-gas component is nitric oxide, with smaller amounts of nitrogen dioxides, nitrosyl chloride, nitrogen, and chlorine. The presence of more than a few per cent hydrogen in an oxidizing gas mixture might provide an explosion hazard. In reagents having a total initial acidity of 7 moles/liter, hydrogen increased from a few tenths of a per cent to about 3 per cent as the hydrochloric-nitric ratio increased from 0.4 to 6, whereas nitrous oxide in the gas evolved similarly increased from a few tenths of 1 per cent to almost 10 per cent. Minor variations occurred during the course of a dissolution. Both hydrogen and nitrous oxide concentrations generally were lower with a deficiency of reagent. It was concluded that careful control of reagent composition should be exerted to minimize hydrogen and nitrous oxide production.

Hastelloy X, used as cladding for the urania-beryllia pellets of the Gas-Cooled Reactor Experiment (GCRE) fuel, can also be dissolved in nitric-hydrochloric acid mixtures. This is a high-nickel alloy containing chromium, iron, and molybdenum. Oak Ridge work[7] suggests the use of a 2*M* nitric acid–4*M* hydrochloric acid mixture to dissolve Hastelloy X.

Total Dissolution of Fuel Material

Dissolving Aluminum-Clad Fuel. Certain foreign reactors utilize MTR type aluminum fuel elements containing uranium enriched only to the 20 per cent level in U^{235}. The intermediate enrichment requires a high total uranium concentration (up to about 48 wt.% of the element); the high concentration prevents the use of simple cladding alloy, and consequently the uranium is present as a uranium dioxide-bearing matrix which may contain silicon in an amount equivalent to 3 wt.% of the element.

Earlier plans to process the 20 per cent enriched uranium–aluminum alloy fuels at Oak Ridge led to the development of a modified tributyl phosphate (TBP) extraction process for recovering uranium and plutonium.[4] The proposed process was one specifically adapted to existing Oak Ridge facilities and planned modifications and was generally similar to one used at the ICPP for highly enriched uranium–aluminum alloy fuels,[8] except for the use of TBP throughout, rather than having TBP and hexone cycles, and for a conventional provision for plutonium recovery.

A particular feature of the Oak Ridge process is the provision for the removal of silica from the solution resulting from dissolving the fuel in 7.5*N* nitric acid. This is a modification of a gelatin treatment and filtration process developed at Savannah River.[9] The dissolver product (1.5*M* aluminum nitrate, 1.3*M* nitric acid, with about 0.4 g of silicon per liter) is cooled to 85°C, $\frac{1}{100}$ volume of 1 per cent gelatin solution is added, and the whole is digested for 1 hr at 85°C to coagulate the silicon. Celite filter aid is added, and the mixture is filtered through a 30-mesh Ottawa sand bed precoated with Celite

filter aid. The cake is washed with a volume of 0.1*M* nitric acid equal to about one-fifth the feed volume to remove uranium and plutonium. In scouting experiments, untreated feed equilibrated with an equal volume of 6 per cent TBP in Amsco 125-82 diluent formed a fairly stable emulsion, whereas treated and filtered feed settled to a clear interface in about 20 sec. Uranium and plutonium losses to the filter cake were negligible.

An additional feature of this proposed process for partially enriched fuels is the addition of 0.05*M* boric acid to the dissolving reagent to prevent attainment of criticality in a batch dissolver that is not geometrically limited. It was determined that boric acid was not lost from the dissolver solution, either during dissolution or during feed coagulation and filtration.

Recovery of rare gases by low-temperature fractionation or adsorption from the off-gas produced by dissolving aluminum fuels in nitric acid requires removal of nitrous oxide from the gas stream. Unlike nitric oxide and nitrogen dioxide, nitrous oxide cannot be removed by caustic scrubbing. Although nitrous oxide can be removed by reduction with hydrogen over a palladium catalyst, followed by dehydration,[10] direct catalytic decomposition would eliminate both the hazard of hydrogen and its cost. Palladium, platinum, and rhodium are suitable decomposition catalysts, of which the last works best at lower temperatures. A catalytic bed was provided to test decomposition effectiveness at the ICPP gas recovery system.[11] The rhodium catalyst consisted of $\frac{1}{8}$-in. alumina cylinders containing 0.5 wt.% rhodium on the surface of the alumina. Since the reaction is strongly exothermic, provision must be made for temperature control, particularly when the initial nitrous oxide concentration is quite high. The most successful test was carried out for 15 days on a gas that initially contained 14 to 20 per cent nitrous oxide to yield a product containing less than 0.05 per cent nitrous oxide. Reactor outlet temperatures varied between 1300 and 1500°F. It appeared that average reactor temperatures somewhat higher than those predicted by batch kinetic data were required.

Dissolving Zirconium-Rich Fuels. Various methods of preparing zirconium-uranium alloys for recovery of uranium by extraction were recently reviewed by Gens.[12] The uses of ammonium fluoride, hydrofluoric acid with oxidizing agents, nitric-hydrofluoric acid mixtures, and gas-phase hydrochlorination were discussed.

Fuel elements for the TRIGA reactor developed by the General Dynamics Corporation are a complex assembly of a uranium–zirconium hydride core (8 per cent uranium), aluminum-samarium burnable-poison disks, graphite plugs, and 30-mil aluminum cladding. The uranium is 20 per cent enriched. The aluminum cladding and poison disks can readily be removed by dissolving in caustic and sodium nitrate, and the graphite plugs can be mechanically removed or disintegrated with nitric-sulfuric acid mixture. At Oak Ridge, studies have been made of dissolving the core in ammonium fluoride solutions in which zirconium hydride dissolves about as well as does zirconium.[13] The high uranium content requires the use of a relatively large ratio of ammonium fluoride. It is proposed to dissolve the fuel element, which weighs 2.7 kg after removal of aluminum and graphite, in 34.8 liters of boiling 5.4*M* ammonium fluoride containing 0.3*M* ammonium nitrate. During dissolution, 8.4 liters of 1*M* hydrogen peroxide are added to maintain uranium in solution in the hexavalent state. To prepare a feed suitable for solvent extraction, about 1.4 volumes of 1.4*M* aluminum nitrate containing 1.6*M* nitric acid are added. Core dissolution is estimated to require about 11 hr since the element has a diameter of 1.42 in. Even with ammonium nitrate present, the off-gas produced contains about 10 per cent hydrogen. Consequently, consideration was given to omission of ammonium nitrate.[14] Tests with both TRIGA fuel and Shippingport Pressurized-Water Reactor (PWR) seed fuel (2.5 per cent uranium in zirconium) showed that foaming was increased somewhat, but was not serious, and that the dissolution rates were the same as in the presence of ammonium nitrate.

The core 2 seed for the Shippingport PWR contains wafers of mixed zirconium and uranium dioxide (34 per cent uranium dioxide, highly enriched) clad with Zircaloy-4. ORNL, in studying means for dissolving the wafers, has found that 9*M* and 12*M* ammonium fluoride solutions attack the wafers very slowly but that 6*M* to 15*M* hydrofluoric acid attacks the wafers at rates[13] of 1.0 to 3.3 mg/(cm^2)(min).

A report has recently been issued[15] describing previously discussed results[16] on the carry-

ing of fission products in the precipitation of barium fluozirconate from solutions of zirconium alloys in hydrofluoric acid.

Electrolytic Dissolution. At Savannah River and at the ICPP, electrolytic methods are of increasing interest for processing power-reactor fuels since they potentially provide a general means of attacking a wide variety of metals and alloys with the use of reagents little more corrosive to stainless steel than nitric acid. Slansky and others have recently summarized work at the ICPP on this technique.[17] Total dissolution of stainless-steel-clad uranium dioxide elements, such as those used in the Yankee reactor, as well as of stainless steel–uranium dioxide matrix fuel like that used in the SM-1 [formerly called the Army Package Power Reactor (APPR)], can be accomplished by electrolytically attacking the stainless steel in moderately concentrated nitric acid. A variety of other high-temperature-resistant alloys can also be dissolved—Inconel X, Hastelloys C and F, Kanthal D and A1, Nichrome, Carpenter 20, Illium R, and others—with only small residues of molybdenum, niobium, silicon, or carbides. Generally, the formation of such minor residues does not interfere with bulk metal dissolution. High-silicon irons such as Duriron and Durichlor are not dissolved. Extensive studies have also been made on the electrochemical behavior of iron and stainless steel in nitric acid, on thermal effects, and on the contact resistance and mechanism of action of valve type anode metals. Recent work on new electrolytic dissolver concepts includes the use of the so-called "series dissolver," in which neither electrode is in contact with the dissolving metal.[18]

In laboratory tests at Savannah River,[19] four irradiated (1900 Mwd/ton) fuel rods of the N.S. *Savannah* reactor type were dissolved electrolytically using a perforated niobium anode in 7*M* nitric acid. The rods were 10 in. long by 0.5 in. in diameter, with a 25-mil stainless-steel cladding over a uranium dioxide core. Dissolutions were stopped after all uranium dioxide and 60 per cent of the stainless steel had dissolved. The dissolver solution, containing silica and a suspension of Fe_3O_4 and stainless steel, was diluted to 0.6*M* uranium concentration and 30 g of stainless steel per liter for Purex type extraction with 10 per cent TBP in Ultrasene. Decontamination factors of better than 10^4 were obtained in one cycle for both uranium and plutonium.

In other work at Savannah River, a 5000-amp semiworks-scale electrolytic dissolver has been installed and operated as described in the section on Plant Design, Instrumentation, and Equipment Development (page 19 of this issue).

Since boiling nitric acid solutions of stainless-steel metals may be undesirably corrosive to stainless-steel vessels, consideration has been given to conducting electrolytic dissolution of stainless steel somewhat below the boiling point of the dissolving reagent. In the case of stainless-steel-clad uranium dioxide, a question arises as to the rate at which the uranium dioxide is dissolved at a reduced temperature. Tests at Savannah River[20] showed that at 90°C uranium dioxide would dissolve at least as rapidly in nitric acid up to a 6*M* concentration as at the boiling point. The presence of 12 g of stainless steel per liter in the dissolving reagent increased the rate at which uranium dioxide dissolved by at least 50 per cent.

The speed with which stainless steel is dissolved electrolytically in nitric acid at low temperatures has suggested that thin stainless-steel fuel jackets might be removed by this means without major loss of uranium dioxide core material to the solution.[17] Measurements of the dissolving rate of uranium dioxide particles indicated that losses of uranium dioxide might not exceed a few tenths of 1 per cent if the cladding were removed by electrolyzing in 0.5*M* nitric acid at temperatures below 25°C. The possibility of cutting tubular cladding electrolytically, by using a hollow needle cathode which directs a fine stream of electrolyte against the tubing, was also indicated.

To extend the application of electrolytic dissolving, attempts have been made to develop processes for zirconium-clad and zirconium alloy fuels on this basis. Although zirconium is anodically attacked and disintegrated in nitric acid, a major fraction is not dissolved but remains as an oxide sludge which spalls off the metal surface. When uranium alloys are so treated, only a portion of the uranium dissolves in the acid. Investigations at Savannah River[20] have shown that 20 to 60 per cent of the uranium from zirconium–low uranium alloys is retained in the oxide derived from both epsilon and delta alloy phases in the uranium-zirconium system. X-ray-diffraction examination of zirconium dioxide sludge derived from zirconium–

10 wt.% uranium alloy indicated that a double oxide of zirconium and uranium was present.

Dissolving Other Nonmetallic Fuel Materials. Fuels for high-temperature reactors include carbides and various graphite and ceramic oxide compositions which provide unusual problems in dissolution or disintegration. In use, these materials may or may or may not be contained in metallic containers, whose removal may be effected by other means.

ORNL[14,21] reports that crushing of uranium dioxide pellets (PWR blanket) increases the dissolution in nitric acid. For 7*M* nitric acid the peak uranium loading was increased from 375 to 500 g/liter. For 4*M* nitric acid the spread between maximum and minimum uranium loading in the product was increased, 400 to 150 g/liter for crushed pellets versus 375 to 225 g/liter for whole pellets.

Instantaneous dissolution rates for these uranium dioxide pellets under simulated inclined-drum rotary leacher conditions in boiling dissolvent analyzing 2*M* to 8*M* nitric acid–0*M* uranium and 5*M* to 2.5*M* nitric acid–2*M* uranium were correlated by

$$\log R = -0.28 + 0.13\,(M\ \mathrm{U}) + [0.18 + 0.62\,(M\ \mathrm{U})^2]M\,\mathrm{H}^+$$

where R is the rate in mg/(cm^2)(min) based on the superficial surface area of right cylindrical pellets.

Arc-melted uranium monocarbide–plutonium monocarbide was dissolved at Los Alamos[22] in 13*M* nitric acid containing 0.05*M* hydrofluoric acid to yield a solution from which both uranium and plutonium were recovered by TBP extraction with negligible losses. Oak Ridge has reacted uranium monocarbide with 4.4*M* nitric acid to produce strongly colored solutions from which uranyl ion was sorbed on a cation resin and the strongly colored species was sorbed on an anion resin.[14,21]

Oak Ridge studies[7] have indicated that thoria, mixed or coprecipitated in urania-thoria, can be leached efficiently by 13*M* to 21*M* nitric acid from ground graphite fuel bodies which have not been graphitized after fabrication, only if the acid contains a small amount (0.04*M*) of fluoride. From graphitized bodies, 7 to 15 per cent of the thoria was not recoverable by two acid leaches and four water washes. Recovery of urania was similar except that the presence of fluoride in the nitric acid was unnecessary for its extraction. In later work on the use of 90 per cent nitric acid for disintegration of irradiated graphitized fuels containing 3 and 12 per cent uranium,[13] uranium recovery was nearly quantitative, but a large part of the zirconium, cerium, cesium, and ruthenium fission products remained in the residue. Combustion of the fuel and leaching of the ash resulted in volatilizing about half the ruthenium but retaining other fission products mostly in the ash.[21] Leaching of graphite containing alumina-coated uranium dioxide particles resulted in very little leaching of the uranium.[14]

In studies of uranium extraction from high-fired 70 per cent urania–30 per cent beryllia pellets, as used in the GCRE, a 5-hr treatment with boiling 6*M* to 13*M* nitric acid was found at Oak Ridge[13] to be effective in recovering more than 99 per cent of the uranium, while only about half the beryllium dissolved. Uranium was also recovered almost completely from a sintered mixture of 4 per cent alumina and 96 per cent urania by boiling 10*M* nitric acid.[7] From similar pellets with 75 per cent alumina, only about half the uranium was leached.[21]

Fuel Preparation by Nonaqueous Methods. Although nonaqueous processing methods are discussed in greater detail in a later section of this Review, certain techniques are particularly aimed at preparing fuels for solvent extraction, and others are applicable for this purpose. These include a modified Zircex process for hydrochlorination of zirconium-uranium alloys[23] and an application of the Zircex process to uranium–10 wt.% molybdenum alloys.[24] These processes are discussed in Sec. III.

Zirconium may also be volatilized as the tetrachloride from alloy fuels by reaction with molten lead chloride. Uranium may be leached from the salt by nitric acid for subsequent solvent extraction. Development of this procedure, known as the Alloy Reguline Chloride Oxidation (ARCO) process, was described recently.[16] Further work has indicated that hydrochloric acid may not be substituted for nitric acid to leach uranium from the salt since losses of uranium are excessive.[25] At 520°C, thorium has been found to dissolve in lead chloride at a rate of 9 mg/(cm^2)(min).

Solvent-Extraction Processes

For the past 10 years, organic solvent-extraction processes have been the principal means for recovering and purifying uranium and plutonium from reactor fuels. The originally important oxygenated hydrocarbon solvent methods have largely been supplanted by phosphate ester processes, although the applications of both types of solvents have been broadened and new solvents have been introduced. In addition to studies to improve and extend the usefulness of solvent processes, the radiation and chemical behavior of the solvents and diluents are problems of major importance.

Studies and Modifications of Purex Type Processes

In the Purex process, uranium and plutonium are extracted from a nitric acid solution by TBP in a hydrocarbon diluent, separated by reducing the plutonium and extracting it from the organic solution under mildly acid conditions where uranium is poorly transferred, and the uranium finally is recovered by extracting with water. Normally, a ferrous salt is used for plutonium reduction, and a nitrite-destroying agent such as sulfamic acid is used to prevent reoxidation of the plutonium until it is out of the extraction system. These agents end up as iron sulfate in the process waste stream. At the Savannah River Plant, the use of ferrous sulfamate results in about 100 lb of solid waste per ton of uranium processed.[26] Consequently, efforts have been made to find an alternate plutonium reductant system which would not add to the solid content of the process waste. English workers using uranous ion in typical Purex process conditions found it unsatisfactory because of excessive contamination of the plutonium product with uranium.[27] Tests at Savannah River on the use of U(IV) nitrate, stabilized with hydrazine, indicated that excessive amounts of U(IV) were required to achieve the desired plutonium separation. These observations led to the assumption that U(IV) was being oxidized rapidly in the organic phase.

Slade at Savannah River[26] has studied the oxidation of U(IV) in nitric acid solution by nitrous acid and by oxygen. Uranium was reduced electrolytically in the presence of hydrazine. It was indicated that U(IV) has adequate stability for use as a plutonium-reducing agent. The half time for oxidation of unstabilized U(IV) by 0.025 *M* nitrous acid was 3 to 4 hr in either 30 per cent TBP or nitric acid solution; in 30 per cent TBP, oxidation by air required about 15 hr before appreciable loss of U(IV) occurred. It was also determined that, for acidities less than about 3 *M* nitric acid, distribution coefficients for U(IV) into 30 per cent TBP in Ultrasene were about one-tenth the values for U(VI) and that, for normal flow ratios, essentially all the U(IV) would be recovered with the U(VI) from the partition contactor. If U(IV) is introduced to the contactor prior to the organic stream, much of it would be picked up in the latter phase before it could be effective. It was suggested that it would be preferable to introduce U(IV) shortly after the organic stream.

Oak Ridge is continuing to study modifications of the Thorex process, which recovers thorium and uranium with diluted TBP, in which acidic conditions are employed to improve ruthenium decontamination. The particular application of interest for this process is the processing of Consolidated Edison reactor fuel (95 per cent thoria–5 per cent urania). The acid Thorex process[7,13] is presently quite complex in respect to the number of streams fed to the extraction-scrubbing contactor, since two scrubbing streams (5 *N* nitric acid and phosphoric acid–ferrous sulfamate) are added at separate points and an additional salting stream of 13 *N* nitric acid is introduced at an intermediate point in the extraction section. The feed stream remains slightly acid-deficient but is pretreated with sodium bisulfite. The extractant is 30 per cent TBP in an Amsco diluent.

In laboratory batch countercurrent and mixer-settler studies, marked improvements in decontamination have been obtained for a number of variations of the acid Thorex process as compared to the older acid-deficient process. The ruthenium decontamination factor has generally been 1000 or more (and up to 35,000), except when salting acid was added at the feed stage in an attempt to simplify the process, as compared to 730 or less for the acid-deficient process.

Russian workers have studied the extraction of chromium ions by TBP solutions.[28] Trivalent chromium is very little extracted. Hexavalent chromium is extracted as chromic acid with a solvation number of 3. The following relation

represents the distribution data:

$$\frac{(H_2CrO_4 \cdot 3TBP)_{org.}}{(H_2CrO_4)_{aq.}(TBP)^3_{org.}} = 0.535$$

Solvent Degradation and Treatment

Hycrocarbon solvents are generally used in Purex type extraction processes to dilute the phosphate ester complexing agent in order to reduce viscosity, to obtain a density for the solvent mixture which will provide an adequate difference in density between it and the aqueous phase, and to limit the concentration of heavy metals which can be complexed in the organic phase. The diluents used must be stable to damage from both process chemicals and radiation effects. Highly paraffinic kerosene-range hydrocarbon mixtures have been used most because they combine stability with reasonably low viscosity and reasonably high flash point. At Hanford, continued studies to evaluate alternate diluents were reported. Potential diluents for TBP in the Purex process were classified into the following groups:[29]

1. Normal paraffins, such as synthetic dodecane (Adekane 12), and fractions isolated by urea treatment.

2. Nonaromatic petroleum fractions: Shell E2342, Bayol-D, Ultrasene, Supersol, Shell 16550, and Shell 82000. The composition of these varies from 60 to 70 per cent naphthenes plus 5 to 10 per cent normal paraffins in Shell E2342 to 20 to 30 per cent naphthenes plus 50 to 60 per cent normal paraffins in Shell 82000. Branched hydrocarbons probably make up the balance. The naphthene fraction is fairly reactive toward nitric or sulfuric acid, and chemical stability is not appreciably improved by a simulated acid degradation–caustic cleanup cycle.

3. Highly aromatic fractions: Penola 100 and Amsco D95E1.

4. Synthetic alkylates produced by polymerization and hydrogenation of short-chain olefins, copolymers, etc.: Soltrol 170, Amsco 125, and Amsco 450.

The chemical stability of the paraffins is expected to decrease in the order: normal, branched, and cyclic. Compounds with tertiary hydrogen atoms are assumed to be particularly susceptible to degradation, and the nitration of carbon atoms having an adjacent hydrogen for enolization may be especially undesirable. On this basis, compounds having a structure $-CH_2CR_2-$ may be particularly stable. Because of the many factors influencing stability and diluent behavior, the importance of a use type test for diluent evaluation was emphasized.

A comparison of behavior of three diluents in simulated service illustrated the complexity of diluent evaluation.[30] Samples of Shell E2342, Soltrol 170, and dodecane containing 30 per cent TBP were washed with sodium carbonate, equilibrated with $3M$ nitric acid containing $0.05M$ sodium nitrite, and then irradiated to a level of 10^8 r using a Co^{60} source. The irradiated solvents were then washed successively with equal volumes of (1) permaganate-carbonate solution, (2) $1M$ nitric acid, (3) 3 per cent sodium carbonate, and (4) $1M$ nitric acid. The washed solvents were then used to carry out simulated Purex type extraction-scrubbing-stripping operations, for which distribution and decontamination data were obtained. Solvent containing the used Shell E2342 diluent extracted four times as much activity as those containing used Soltrol and dodecane, but the extracted activity was stripped more easily from the latter solvents. Therefore the over-all decontamination factors for uranium were less with Soltrol and dodecane than with the Shell diluent. For all three diluents the amount of activity extracted was relatively high in accordance with the high exposure level. In another aspect of diluent stability studies, the relatively paraffinic Shell 82000 diluent was distilled to obtain fractions which were principally the normal C_{10}, C_{11}, and C_{12} hydrocarbons, respectively. After nitric acid degradation of the fractions, a use type test showed poorer performance as the molecular weight increased, but all fractions were superior to unfractionated Shell 82000 diluent.

At Savannah River, studies of diluent degradation have been concerned with the behavior of pure hydrocarbons in complexing zirconium after chemical treatment or irradiation.[31] The compounds were degraded by exposure to nitric acid containing nitrous acid, either by holding seven days at 70°C or by irradiating to 10^7 rep from irradiated fuels for a few hours at a maximum of 60°C. Evaluation of stability was carried out after washing the degraded compound by adding 30 per cent TBP and measuring the "Z test" value.[32] The Z test is a measure of the tendency of the material

Table II-1 STABILITY OF PURE HYDROCARBONS TO ACID AND IRRADIATION DEGRADATION[31]

(Relative Z-test value after compound had been in contact with equal volume of 4*M* nitric acid–0.1*M* nitrous acid for conditions stated. Ratio of Z number of compound to Z number of dodecane: stable, < 2; moderately unstable, 2 to 8; and unstable, > 8.)

Class of Compound	Name of compound	Radiolytic stability after exposure to 10^7 rep	Chemical stability after 7 days at 70°C
Normal paraffin	*n*-dodecane	Stable	Stable
Isoparaffin	2,2,4,6,6-pentamethyl heptane	Stable	Stable
Isoparaffin	2,2,4-trimethyl pentane	Stable	Stable
Isoparaffin	2,3,5-trimethyl hexane	Stable	Stable
Cycloparaffin	*n*-butyl cyclohexane	Stable	Stable
Cycloparaffin	*cis*-decahydronaphthalene	Stable	Stable
Cycloparaffin	*trans*-decahydronaphthalene	Stable	Stable
Cycloparaffin	cyclohexane	Stable	Stable
Olefin	1-undecene	Unstable	Unstable
Olefin	1-dodecene	Unstable	Unstable
Olefin	1-hexadecene	Unstable	Unstable
Olefin	2,5-dimethyl-3-hexene		Unstable
Aromatic	Isobutylbenzene	Stable	Stable
Aromatic	*sec*-butylbenzene		Stable
Aromatic	1-methyl-4-tert.-butylbenzene	Stable	Moderately unstable
Aromatic	1,3-dimethyl-5-ethylbenzene	Stable	Moderately unstable
Aromatic	1,2-dimethylbenzene	Moderately unstable	Moderately unstable
Aromatic	1,2,4,5-tetramethylbenzene	Stable	Stable
Cycloaromatic	Tetrahydronaphthalene	Moderately unstable	Unstable
Cycloaromatic	Indane	Unstable	Unstable

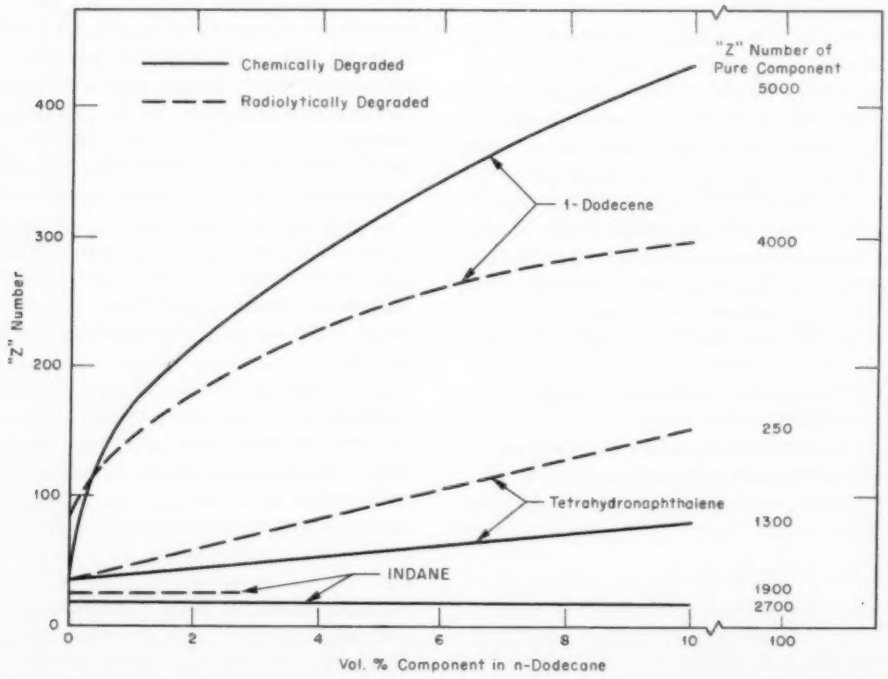

Fig. II-2 Comparative stabilities of hydrocarbon mixtures.[31]

to form ligands that complex zirconium. The test is conducted by equilibrating the sample with a solution of zirconium tracer, following which the sample is scrubbed with nitric acid and the zirconium retained is measured.

Olefins and certain aromatic hydrocarbons in the molecular weight range of kerosene were found to be major precursors of zirconium ligands. Partially aromatized polynuclear structures and 1-olefins of a straight chain type were highly unstable. Alkylbenzenes tested ranged from stable to moderately unstable. Normal, iso-, and cycloparaffins were comparatively stable, as summarized in Table II-1.

The stability of certain hydrocarbon mixtures was also investigated. The instability of mixtures of 1-dodecene and *n*-dodecane was a direct function of the concentration of 1-dodecene, and the stability of dodecane could be reduced to that of Ultrasene (rated as moderately stable) by as little as 0.25 per cent of 1-dodecene. The stabilities of mixtures of partially hydrogenated polynuclear aromatics and *n*-dodecane were not simple functions of aromatic content, and in the case of dodecane-indane mixtures, completely anomalous results were observed since dilute indane mixtures were as stable as pure dodecane. Figure II-2 shows the observed Z values for dodecane mixtures as well as the values for the pure compounds.

Propst at Savannah River[33] has observed that the Z-test values are correlated with polarographic waves found for solvent mixtures in a lithium chloride–benzene–methanol electrolyte. Diffusion currents measured for a wave at −1.1 volts appeared to be related to the degree of solvent degradation. Similar reduction waves were found for 1-nitropropane, 2-nitropropane, and *n*-butylnitrite.

Chemical and radiation effects on the TBP complexing agent are also of major importance in the problem of solvent deterioration. Moffat and Thompson[34] at the ICPP have studied the rates and products of decomposition of diluent-free TBP during and after contact with nitric acid and zirconium nitrate solutions. Volatile decomposition products were determined by gas-liquid chromatography. The reaction of TBP with nitric acid in the organic phase was found to involve dealkylation, with *n*-butyl nitrate being the principal volatile product. With an increase in organic phase acidity from 0.9 to 2.9, the rate constants for the first-order reaction at 50°C increased from 3.4 to 6.7×10^{-5} hr^{-1}. The rates of reaction were essentially unchanged by keeping the TBP in contact with nitric acid or by removing it from acid contact.

Zirconium nitrate is complexed in TBP solutions as a compound of the form: $Zr(NO_3)_4 \cdot 2TBP$. In TBP solution a reaction occurs to produce a relatively insoluble crystalline zirconium organic phosphate, presumably $Zr(NO_3)_2(DBP)_2$. Again, butyl nitrate is the volatile product formed. This over-all reaction is much more rapid than the reaction of TBP with nitric acid, as the unimolecular rate constant at 50°C for an initial zirconium concentration of about $0.2M$ is about 5.0×10^{-2} hr^{-1}. Since the solid does not precipitate from the TBP solution until after the TBP-zirconium reaction is complete (three days at 50°C), it appears that the reaction occurs in two stages with the formation of a soluble intermediate phosphate $Zr(NO_3)_3DBP$.

At 70°C the phosphate precipitate initially formed is converted in a few days to a colloidal material, and the butyl alcohol concentration increases. The course of this subsequent reaction has not been determined.

Decomposition of TBP to dibutyl and monobutyl phosphates can result in the production of various salts whose solubilities may be limited, and which may have other effects on extraction processes. Davis at Oak Ridge has measured solubilities of the dibutyl and monobutyl phosphates of uranium and ferric iron in typical TBP extraction-process solutions which had been equilibrated with the corresponding immiscible phases, with results[35] as shown in Table II-2.

These solubility data confirm the tendency for TBP degradation products to retain uranium in the organic phase. It is also noted that minor concentrations of dissolved iron (as low as 100 ppm) should prevent DBP from retaining uranium in the organic phase due to the precipitation of ferric dibutyl phosphate. All these compounds appear to be interface seekers when their solubilities are exceeded, since dense flocs were formed in the solutions.

At the ICPP, solubilities of uranium, aluminum, and zirconium dibutyl phosphates have been determined in pure hydrocarbon diluent (Amsco 125-90W). At 25°C the solubility[36] of the uranyl compound was $4 \pm 2 \times 10^{-5}M$, that of the aluminum compound was $1.5 \times 10^{-4}M$, and that of an impure zirconium compound was $8 \times 10^{-3}M$. The solid uranyl and aluminum

compounds were found to be thermally stable to 190 and 220°C, respectively.[37]

Since, for economic processing, used and degraded diluted TBP solvents must be recycled to the process, methods of solvent treatment to remove degradation products have been extensively investigated. Largely, such methods have involved washing with alkaline aqueous solutions (or treating with solid alkaline materials) aimed to remove the acidic products of TBP hydrolysis. It is apparent that neither the volatile organic products resulting from TBP decomposition nor the products of diluent degradation are likely to be removed by such methods. Oxidizing agents, such as permanganate, in aqueous solutions have been employed to supplement the removal of acid products. Such agents presumably help to remove both complexed fission products and possibly undesirable materials formed from the diluent. In England some preliminary studies have been made on the use of organic bases for solvent treatment.[38] It was desired to find a low-viscosity liquid, immiscible with the TBP-kerosene system, which would not preferentially extract TBP. Candidate materials tested included mono-, di-, and triethanolamine, several aminopropanols, ethylene diamine, and *N*-hydroxymethyl-diethanolamine. These agents were tested for their ability to reduce the tendency of degraded solvent to complex hafnium (the test used was much like the Z test, referred to above), as well as to remove the hafnium. The solvent, consisting of 20 per cent TBP in an odorless kerosene, was degraded in the laboratory by refluxing with 3*M* nitric acid for periods up to a week. Triethanolamine and monoisopropanolamine appeared most suitable for the removal of uncomplexed materials from degraded solvents, while monoethanolamine and 3-aminopropanol removed hafnium complexes most efficiently from degraded solvents. However, the testing was very limited, and other factors, such as ease of separation and cost, must be evaluated.

Table II-2 SOLUBILITY OF URANYL AND IRON DIBUTYL AND MONOBUTYL PHOSPHATES[35]

Solvent	Solubility, grams of metal per liter			
	Uranyl dibutyl phosphate, g of U	Uranyl monobutyl phosphate, g of U	Ferric dibutyl phosphate, g of Fe	Ferric monobutyl phosphate, g of Fe
Distilled water (saturated with 30% TBP)	0.004	0.05	<0.001	<0.01
30% TBP in Amsco 125-W (saturated with distilled water)	14	~10	<0.01	<0.01
1.0–1.1*M* nitric acid (saturated with 30% TBP)	0.27	27	0.01	1–3
30% TBP in Amsco 125-W (containing 0.2–0.25*M* HNO_3)	117	100	<0.01	1.3

Ion-Exchange Processes

Although ion-exchange processes have seldom been used for primary recovery and decontamination of valuable materials in used nuclear fuels, a considerable amount of process research and development has been carried out to show their applicability for such purposes. The principal applications of ion-exchange resins in fuel processing, however, have been for isolation, final purification, and concentration of uranium and plutonium and for fission-product recovery. The latter subject is discussed in the section on Waste Disposal. The development of continuous ion-exchange process equipment is described in the section on Plant Design, Instrumentation, and Equipment Development.

Uranium and Plutonium Processing by Ion Exchange

At the Oak Ridge Y-12 plant, uranium reclamation operations are carried out for a wide variety of process materials. Nitrate solutions are usually obtained. Because of possible economic advantages, the use of anion resin exchange in such recovery operations was explored. Googin and others[39] have presented extensive equilibrium and kinetic adsorption data for uranium from nitrate solutions, containing various other metal ions, onto Dowex 21K resin, together with some similar data for Dowex 1 resin of varying percentage cross-linkage. Their work was done for the most part with rather

coarse resin particles (50 to 100 mesh, and 16 to 20 mesh) adaptable to use in continuous ion-exchange devices. Other cations present included aluminum, iron (ferric), calcium, zirconium, thorium, and ammonium with total nitrate concentrations ranging up to 9*M*. Effects of small amounts of sulfate and chloride in nitrate solutions were also evaluated. Although no processes were described, it was concluded that uranium adsorbability from approximately 2*M* aluminum nitrate solutions is large enough to make recovery and purification feasible, and that stripping from the resin with dilute nitric acid could be accomplished. Attainment of equilibrium was very slow with the 16- to 20-mesh resin particles but could be speeded by using smaller resin particles, higher temperatures, or proper choice of nitrate salt molarity.

Solutions that contain relatively large amounts of solids cannot be processed in fixed resin beds because the beds are rapidly plugged by the solids. Liquid fluidized or agitated beds permit the processing of such feed streams, since the solids are kept in suspension and removed with the effluent. At Savannah River, studies of plutonium and thorium sorption were made with a contactor in which agitation was effected by stirring at 125 rpm with a flat paddle.[40] In such a device, complete mixing occurs almost instantly. In concentrated nitric acid solutions, thorium has a much lower affinity for anion resins than does plutonium. The chemical performance of agitated beds of Dowex 1 X-4 resin (20 to 50 mesh) was studied, and a method of calculating the performance from nonequilibrium adsorption data was developed. Comparison of the performance of beds of 43 cc volume with a bed 1000 times as large showed that data obtained with the smaller units can be scaled up without difficulty.

In the performance calculation the agitated bed of resin is treated as a single-stage batch contactor in which the liquid and resin are mixed for a time equal to the liquid residence time in the bed. Batch contact data for a corresponding time are used to calculate losses of ions. Subsequent contacts are considered to displace instantaneously the preceding solution, with surface adsorption sites becoming newly available by virtue of diffusion into the resin bead. The loss is then assumed equal to that from the first volume plus that by desorption of an additional fraction of the ions which have diffused into the bead. The loss for the *n*th increment is given by the following equation:

$$C_n = \sum_{j=1}^{n} \left(\frac{C_0 - \sum_{i=1}^{j-1} C_i}{R_j + 1} \right)$$

where

C_0 = concentration of ion in feed solution, mg/liter
C = concentration of ion in effluent, mg/liter
C_n = concentration of ion lost in the *n*th bed volume

Calculation of cumulative losses of plutonium for processing 70 bed volumes of feed indicated that losses would be very high when residence time in the beds is less than 5 to 6 min but are reasonably low at a residence time of about 8 to 10 min. Little or no improvement in recovery is obtained by lengthening the residence time beyond 12 to 15 min.

Thorium can also be sorbed by suitable ion-exchange resins in preference to uranium. At Oak Ridge a synthetic U^{233} product solution containing 25 g of uranium and 0.23 g of thorium per liter in 0.24*N* nitric acid was passed through a bed of Dowex 50W resin at a rate of 0.7 ml/(min)(cm^2). Although 99 per cent of the thorium was removed, only 1 per cent of the uranium was sorbed.[21]

For use in processing highly radioactive materials, ion-exchange resins must be reasonably stable under irradiation. Savannah River workers interested in applying resins to processes where radiation effects might be severe made an evaluation of two cation and three anion resins irradiated in various forms.[41] Total ion-exchange capacity, "salt-splitting" capacity (a measure of the strong-acid or strong-base functional groups), moisture content, and particle size of the resins were measured after various gamma doses up to 2.7×10^8 rads. Infrared spectra were also studied.

Dowex 50W X-12 cation resin was relatively stable to radiation damage. A dose of 2.7×10^8 rads caused no significant change in the total ion-exchange capacity, but the salt-splitting capacity was decreased by 8 per cent. The main source of damage to this resin was the breakage of cross-links in the polymer matrix, with some replacement of sulfonic acid groups by phenolic groups.

Duolite C-10 cation resin was less stable than Dowex 50W. The resin lost 8 per cent of its total capacity and 17 per cent of its salt-splitting capacity after irradiation to 1.5×10^8 rads.

The anion-exchange resin Dowex 1 was severely degraded by a dose of 2.7×10^8 rads with a loss of 58 per cent of its total capacity and 85 per cent in salt-splitting capacity. The strong-base quaternary ammonium groups were replaced to some extent by weak-base groups.

Permutit SK, an anion resin containing pyridine groups, was far more resistant to radiation damage than Dowex 1. After exposure to 2.7×10^8 rads, this resin lost only 8 per cent in total capacity and 55 per cent in salt-splitting capacity.

Radiation effects on ion-exchange resins have also been studied at Oak Ridge. Dowex 50 X-8 in a flow system with demineralized water was exposed to a 10,000-curie Co^{60} source. Total product losses were not linear with radiation dose, being 20 and 85 per cent after exposures of 1.1×10^9 and 5.1×10^9 rads, respectively. The resin darkened, formed aggregates of beads, and fractured.[21]

Precipitation Processes

Aqueous separation techniques involving precipitation as a primary operation are generally avoided since solid-liquid phase separations do not lend themselves well to completely separate recovery of both phases nor to continuous operations. However, such difficulties can be overcome by special techniques when the advantages of precipitation are sufficient, and these methods are applied in special cases.

The TURRET reactor being developed by Los Alamos will use unclad, porous graphite fuel elements impregnated with enriched uranium solutions and heated. The TURRET experiment will include investigating the degree to which low-cost, chemically and mechanically simple fuel-processing methods may be applied to such a fuel.

A proposed method for uranium recycle from TURRET elements involves:

1. Ashing and dissolution, or comminution and leaching, of the graphite.
2. Precipitation of the uranium as the peroxide to accomplish some fission-product separations.
3. Dissolution of the peroxide precipitate in nitric acid to provide a solution for impregnating new fuel elements.

Peroxide precipitation has been investigated using simulated fission-product-bearing solutions and "hot" precipitation experiments using La^{140} to provide the expected radiation intensity. Four simple treatments were compared:[42,43]

1. Precipitation of $UO_4 \cdot xH_2O$ with excess hydrogen peroxide at *p*H 1.5 to 1.7.
2. Preliminary precipitation of fission products with ammonium carbonate at *p*H 8.2, filtration, and precipitation of $UO_4 \cdot xH_2O$ at *p*H 2.7 achieved by acetate buffering.
3. Preliminary precipitation of fission products with ammonium carbonate at *p*H 8.2, filtration, and precipitation of $UO_4 \cdot xH_2O$ at *p*H 1.5 to 1.7.
4. Preliminary carbonate precipitation, filtration, and precipitation of uranium as the diuranate by boiling.

In cold tests the separation of fission products expected to remain in the fuel after reactor exposure was such as to reduce the expected beta activity to 6 to 24 per cent of the starting level, with procedure 3 appearing to be the most effective and the diuranate precipitation the least. Losses of uranium were about 2 per cent by the first technique and a few tenths of 1 per cent by methods 2 and 3. In later hot tests with beta activity simulated with La^{140}, uranium losses increased severalfold.[44] Zirconium appeared to be the principal contaminant of the precipitated uranium in these procedures. It was possible to reduce zirconium contamination markedly by complexing it with tartaric acid during the peroxide precipitation,[45] but uranium losses were increased thereby.[44]

At Oak Ridge a solvent-extraction procedure was applied to recover several hundred grams of Np^{238} remaining in the nonvolatile residue from the fluorination to uranium hexafluoride of recycled uranium trioxide.[9,46] The product, containing small amounts of uranium, thorium, plutonium, fission and corrosion products, and process chemicals, was purified by a precipitation process and partially converted to neptunium dioxide.[47]

Neptunium at a concentration of 3 g/liter in 11*M* nitric acid solution was evaporated to remove excess nitric acid, diluted to 3*M* nitric, and oxidized to the hexavalent state with bromate

at room temperature. Fluorides of thorium, chromium, and plutonium were precipitated by adding hydrofluoric acid and potassium fluoride. After removal of the impurity precipitate, neptunium was precipitated as potassium neptunium fluoride by reduction with sulfur dioxide. The neptunium precipitate was dissolved in 8*M* nitric acid saturated with boric acid and was reprecipitated as the oxalate for conversion to neptunium dioxide by calcination. Recovery was substantially complete after recycle of a small percentage of the product and rework of waste solutions. The product oxide contained a few tenths of 1 per cent of heavy metals, but all other elements were absent or at levels less than 100 to 700 ppm.

Plant Design, Instrumentation, and Equipment Development

The physical and operational features of a continuous countercurrent liquid-solids contactor are reported by Grimmett and Brown from work done at the ICPP.[48] Possible uses for such a column in reactor fuel processing include recovery and concentration of plutonium, separation of specific fission products from waste streams, and leaching of fission products from calcined or solidified radioactive wastes. The five-stage contactor is constructed of 2-in.-diameter Pyrex glass pipe; all other wetted parts are made of stainless steel. The fluidization of the solids is effected by pulsing the column of liquid with a piston type pulser operated at amplitudes up to ½ in. and frequencies up to 2000 cycles/min.

Solids are fed continuously into the top of the column; they then pass from stage to stage and are dischareged into a slurry airlift at the bottom. Liquids are fed in near the bottom of the column, pass through each stage, and are discharged at the top. Special top and bottom sections are designed to facilitate these operations. The stage plates are perforated, and each plate has a layer of ball packing (stainless steel in the reported model). This packing minimizes the passage of solids, is not clogged by solids, and allows the upward passage of liquid.

The column has certain operating characteristics that are determined primarily by the pulse frequency. At least four operating regions can be identified, some of which are characterized by smooth fluidization and the others by turbulent fluidization. In general, an increase in pulse frequency increases the solids flow rate until a maximum is reached near 600 cycles/min, at which point any further increase in frequency reduces the allowable solids flow rate.

The operating characteristics are also influenced by the pulse amplitude, the physical properties of the solids, the configuration and physical dimensions of the column, and to some extent the liquid flow rate. In general, an increase in liquid flow rate decreases the maximum solids flow rate, whereas an increase in pulse amplitude increases the maximum solids flow rate.

A complete determination has not been made of the operating characteristics of all the possible stage configurations and dimensions. However, a few exploratory runs have shown that satisfactory column operation is obtained using a bed depth of 1½ in., a ball packing depth of ¼ in., and a solids downcomer seal depth of ¼ in.

Flow rates of a typical ion-exchange resin up to 150 lb per hour per square foot of column, and up to 300 lb per hour of a calcined alumina per square foot, were obtained while feeding water at rates up to 2000 lb per hour per square foot.

Two ion-exchange systems were studied to determine stage efficiencies; both utilized a cationic concentration of 0.1*N*. One was the system copper-sodium, with sulfate as the common ion, and the other was the system copper-hydrogen, with nitrate as the common ion. Stage efficiencies of greater than 60 per cent are reported. Comparable HTU values were 1.1 to 3.2 in. of resin. Hanford reports on a similar column.[49] This type of contactor offers simplicity of operation (one moving part, the pulser), truly continuous operation, fairly wide range of operating rates, and good possibilities of remote operation.

A Jiggler (jigged-bed continuous countercurrent ion exchanger) contactor is being developed at Hanford as reported in previous Reviews[50] making use of a similar principle. It is reported[51] that the problem of resin flow has been solved by the application of two check valves in the pulser chamber of the Jiggler. These valves in combination with the pulser provide the basic elements of a pump.

Initial experimental evidence indicates that the resin thus moves with a positive displacement action. These values are simple and appear to be dependable, the only moving part being the small plastic sphere activated by the hydraulics of the system.

to 50-mesh resin. This is thought to be more than adequate to overcome backpressure of countercurrent flow of the process stream.

A prototype electrolytic dissolver is reported in two Savannah River progress reports[19,20] and

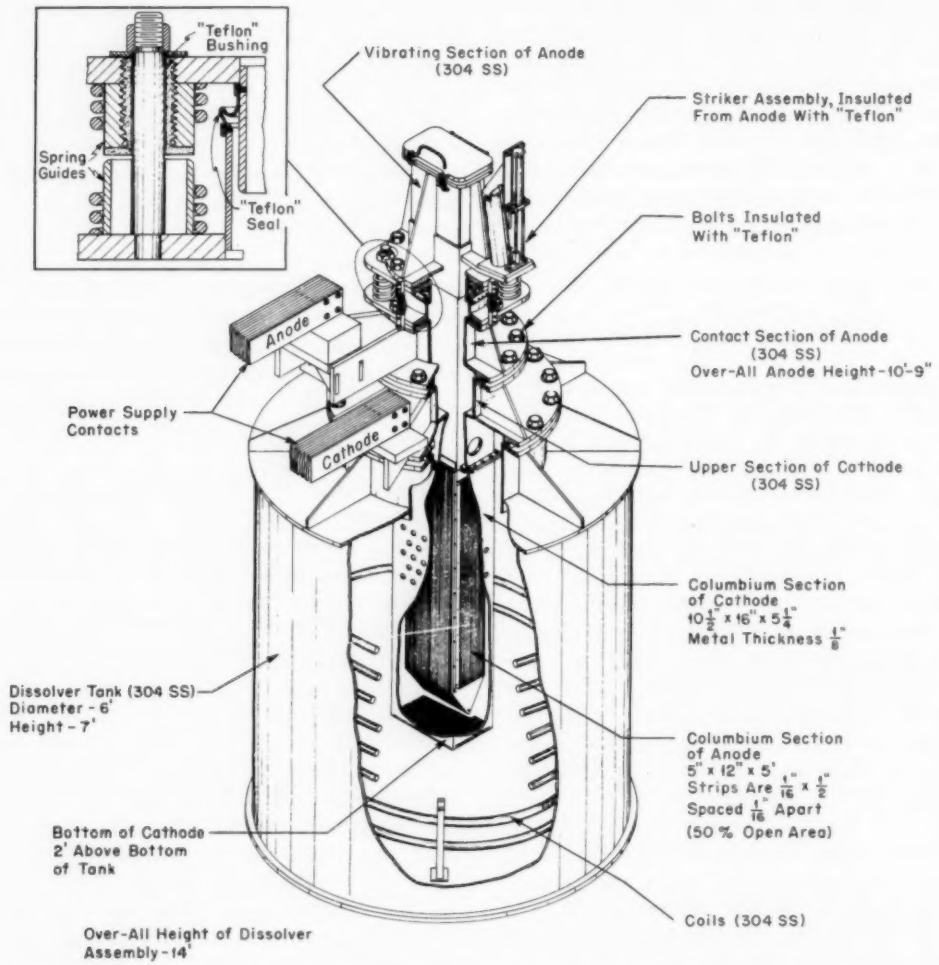
"Teflon" Bushing
Vibrating Section of Anode (304 SS)
Striker Assembly, Insulated From Anode With "Teflon"
Spring Guides
"Teflon" Seal
Bolts Insulated With "Teflon"
Anode
Contact Section of Anode (304 SS) Over-All Anode Height-10'-9"
Power Supply Contacts
Cathode
Upper Section of Cathode (304 SS)
Columbium Section of Cathode 10½" x 16" x 5¼" Metal Thickness 1/8"
Dissolver Tank (304 SS) Diameter - 6' Height - 7'
Columbium Section of Anode 5" x 12" x 5' Strips Are 1/16" x 1/2" Spaced 1/16" Apart (50 % Open Area)
Bottom of Cathode 2' Above Bottom of Tank
Coils (304 SS)
Over-All Height of Dissolver Assembly - 14'

Fig. II-3 Prototype electrolytic dissolving vessel.[19]

Tests of several hours' duration each, with no process liquid being pumped through the system, demonstrate that resin can be pumped readily through 4-in. glass pipe. Slip water was negligible, and the quantity of resin moved appeared to be directly related to the amplitude-frequency product. The arrangement was capable of developing 40 psig while recirculating 20-

is illustrated in Fig. II-3. The 1000-gal dissolver vessel is made of type 304 ELC stainless steel. Provision has been made for measuring corrosion both on the walls of the tank and on the cooling coils. The charge to be dissolved is held in an anode basket made of strips of columbium. A columbium cathode completely surrounds the anode. The dissolver

is designed to operate at 5000 amp at 10 to 30 volts. Teflon is being used as insulation; however, irradiation tests are being run on other materials.

Several experiments seem to indicate possibilities of good operation with only minor changes. Severe arcing damaged the columbium anode ($^1/_{16}$-in. strips). However, replacement with solid $^1/_2$-in. plate has solved this problem. For aluminum and stainless-steel dissolution, corrosion was reported to be less than 1 mil/year. A dissolution rate of 5 lb/hr at an average current of 3500 amp and 11 volts was reported. This was obtained with an initial charge of 200 lb of tubes $^3/_4$ in. in outside diameter and 8 ft long in 4.5*M* nitric acid. After 50 hr of dissolution of stainless-steel rods, the bottom of the modified columbium anode basket appeared to be as smooth as when originally installed. To avoid serious arcing when using the anode hammer to reestablish contact, the current was shut off while hammering.

Construction Materials

In earlier Reviews it was indicated that Hanford was planning to use the Zirflex and Sulfex processes for the decladding of zirconium alloy fuels and stainless-steel fuels, respectively. It had been reported that vacuum-melted Hastelloy F was the preferred construction material; however, it was learned in corrosion testing that self-weldments of this material were subject to moderate preferential attack in boiling Sulfex environments; in addition, Hastelloy F suffered rather severe attack in welds and areas adjacent to welds when exposed to Niflex dissolver solutions.[27] Hanford, with the cooperation of Battelle Memorial Institute, entered into an alloy development program for the purpose of overcoming the sensitivity of Hastelloy F to such local weld penetrations. Tests with the first 12 such alloys are negative; none of the alloys were found to be satisfactory as a filler metal for welding Hastelloy F. However, there was sufficient indication that some of these alloys, if modified moderately, had the potential of being useful as a primary construction material. As a result, a second set of 12 experimental alloys was made by Battelle and tested by both Battelle and Hanford. The Battelle results were reported in a preceding Review.[16] Hanford's corrosion evaluation of these alloys has now been completed, and a topical report has been issued.[52]

The experimental alloys prepared by Battelle had compositions that were similar to the commercial Hastelloy F alloy. In earlier corrosion work, Hanford had concluded that, of the commercial alloys, Hastelloy F had properties that were about optimum for use in both Zirflex and Sulfex decladding processes. Mainly, the effects of varying the contents of molybdenum, copper, titanium, and niobium were explored. The effects of a small variation of chromium content and the inclusion of 25 per cent cobalt were also studied. Analyses of the principal constituents of these materials are shown in Table II-3. The alloys were exposed to a total of 10 different boiling solvents. A listing of the experimental environments together with alloy condition is shown in Table II-4.

Table II-3 CHEMICAL ANALYSES OF PRINCIPAL CONSTITUENTS OF EXPERIMENTAL NICKEL-BASE ALLOYS[52]

Alloy	Composition, wt.%						
	Ni	Fe	Cr	Mo	Cu	Ti	Nb
1	45	23	22	6	1		2
2	45	22	22	6	2		2
3	45	25.5	22	6		0.5	
4	45	25	22	6		1	
5	45	26.5	22	3	2	0.5	
6	45	26	22	3	2	1.0	
7	45	21	22	6	3		2
8	45	20	22	9	1		2
9	45	26	22	3	1		2
10	45	24	22	6	2		
11	45	23	22	6	2	1.0	
12	45	25	22	3	2		2
13	45	29.5	22	1.5		1.0	
14	45	26.5	22	4.5		1.0	
15	45	22	22	9		1.0	
16	45	21	22	9	1	1.0	
17	50	21.5	25	1.5		1.0	
18	50	18.5	25	4.5		1.0	
19	50	17	25	6		1.0	
20	50	16	25	6	1	1.0	
21	50	18.5	25	1.5	3	1.0	
22*	25	20	22	6		1.0	
23*	25	17	25	6		1.0	
24*	25	14	25	9		1.0	

*These alloys also contained 25 per cent cobalt.

Maness at Hanford used two bases of corrosion assessment: weight loss for determining general surface attack, and metallographic eval-

Table II-4 AQUEOUS DISSOLVENTS USED AS STANDARDS FOR CORROSION TESTING EXPERIMENTAL NICKEL-BASE ALLOYS[32]

Dissolvent	Process application
65% nitric acid*	Dissolution of UO_2 fuel
4*M* sulfuric acid	Sulfex—stainless-steel decladding
4*M* sulfuric acid and 20 g/liter dissolved stainless steel†	Sulfex—stainless-steel decladding
6*M* ammonium fluoride‡	Zirflex—zirconium decladding
6*M* ammonium fluoride and 0.5*M* ammonium nitrate*	Zirflex—zirconium decladding
1*M* nitric acid and 2*M* hydrofluoric acid	Niflex—dissolution of stainless-steel- or zirconium-clad fuels
0.25*M* nitric acid and 4*M* hydrofluoric acid	Niflex—dissolution of stainless-steel- or zirconium-clad fuels
3*M* nitric acid and 2*M* hydrochloric acid§	Darex—stainless-steel decladding or dissolution of stainless steel–UO_2 cermet
5*M* nitric acid and 0.5*M* ferric nitrate*	Dissolution of U-Mo alloys

* Alloys tested in both annealed and sensitized conditions.
† Tests conducted with both cold-finger condenser and open-end condenser.
‡ Alloys tested in sensitized condition.
§ Alloys exposed to both liquid and vapors.

uations for subsurface corrosion. A systematic method of data interpretation was used to evaluate the effect of individual alloyed constitutents. The method used is illustrated in Fig. II-4 for data accumulated in the boiling 65 per cent nitric acid environment. Similar analyses were made for each of the dissolvents. Some of the observations made through this technique are indicated below.

65 Per Cent Nitric Acid

1. All sensitized niobium-stabilized alloys containing more than 3 per cent molybdenum were severely attacked.

2. All sensitized titanium-stabilized alloys with less than 6 per cent molybdenum were not attacked.

3. Sensitized titanium-stabilized alloys with 9 per cent molybdenum were severely attacked.

4. Sensitized alloys containing cobalt were severely attacked.

5. Increasing the chromium content from 22 to 25 per cent decreased the general attack of sensitized alloys.

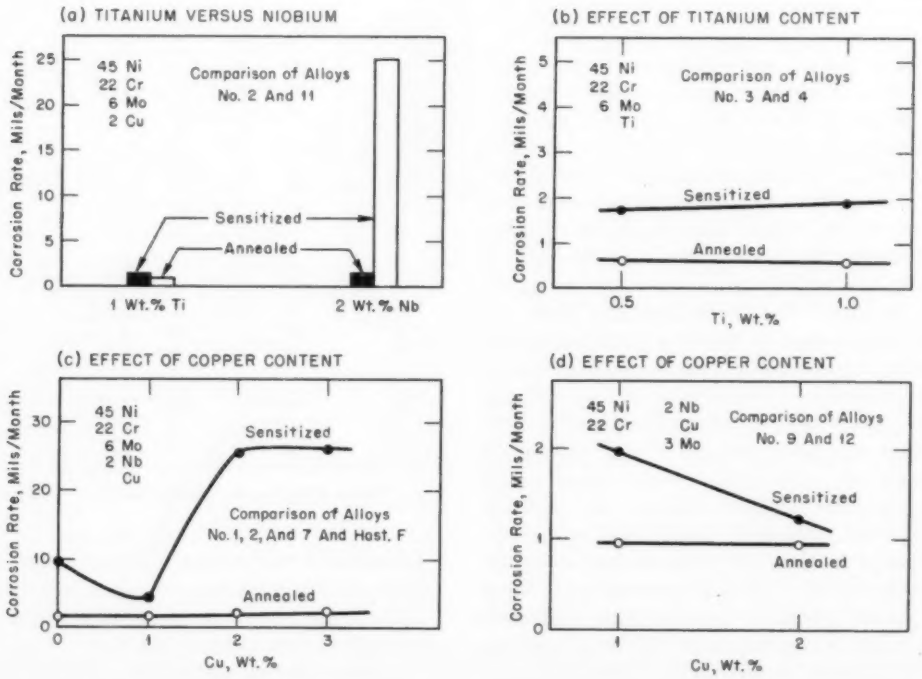

Fig. II-4 Effect of alloy components on corrosion resistance in boiling 65 wt.% nitric acid.[32]

Sulfex Systems

1. Molybdenum and copper contributed heavily to corrosive resistance.
2. One per cent copper reduced the attack substantially in acid not containing dissolved stainless steel.
3. Four per cent molybdenum decreased the attack of alloys substantially in all three Sulfex dissolvents.

Zirflex Systems

1. Molybdenum had a marked beneficial influence.
2. All alloys (except those containing cobalt) showed a lowered resistance to solutions containing nitrate.

Niflex Systems

1. The welds of niobium-stabilized alloys were subjected to severe local attack.
2. The areas adjacent to welds in niobium-stabilized alloys were severely attacked.
3. Titanium-stabilized alloys with 6 per cent molybdenum (with or without 1 per cent copper) showed no preferential attack.
4. Titanium-stabilized alloys containing less than 6 per cent molybdenum had reduced resistance, and some weld-metal attack was observed.
5. Increase of chromium content from 22 to 25 per cent was beneficial.
6. Increased copper content increased general attack moderately.
7. Increasing the molybdenum content from 3 to 6 per cent increased the general attack of niobium-stabilized alloys.
8. Increasing the molybdenum content from 3 to 6 per cent decreased the general attack of titanium-stabilized alloys.

Darex Systems

1. A minimum molybdenum content of 6 per cent was needed for adequate resistance to this environment.

From the corrosion data presented in the report, it is evident that alloys 19 and 20 (Table II-3) and, to a lesser extent, alloys 3 and 4 represent about the best compromise among all the alloy compositions tested. All four of these alloys contain 6 per cent molybdenum and are titanium stabilized. Alloys 19 and 20 contain 25 per cent chromium, and alloys 3 and 4 contain 22 per cent chromium. Of the four, only alloy 20 contains copper.

Note in Table II-4 that the exposures to 4 *M* sulfuric acid containing dissolved stainless steel were conducted with two condenser types, open end and cold finger. The tabular data presented in the report indicate that corrosion rates for the open condenser are a factor of 2 to 15 less than those in experiments conducted with a cold-finger condenser. The difference in these results is apparently associated with the presence of noncondensable gases. The open condenser arrangement is much more conducive to the elimination of these noncondensables. An opposite effect is observed in process environments used for electrolytic dissolution of stainless-steel fuels at Savannah River (see below).

The testing of stainless-steel types 304L and 309SCb as construction materials for the electrolytic dissolution of stainless steel is being conducted at Savannah River. Previous work had indicated that the accumulation of dissolved stainless steel in nitric acid solutions adversely affected the corrosion resistance of austenitic stainless steels. In the past quarter the effect of temperature on these corrosion rates was explored.[20] The results are shown graphically in Fig. II-5. The data indicate that a marked decrease in corrosion rate could be obtained by reducing the dissolution temperature from 113 to 85°C. The feasibility of such a temperature reduction would be determined by an ability to maintain dissolution rates. Several corrosion experiments were conducted with stainless-steel type 304L during actual electrolytic dissolutions of type 304L anodes. The initial dissolvent was 6*M* nitric acid held at a temperature of 85 to 90°C. The concentration of stainless steel at the conclusion of the runs (19- to 24-hr duration) ranged from 21 to 43 g/liter. In six of eight tests, the corrosion rates were less than $3\frac{1}{2}$ mils/year, and the terminal solutions were blue. In the remaining two tests, rates of attack ranged from 8 to 13 mils/year and terminal solutions were yellow or yellow-green. It was concluded that in the latter two tests the nitrogen oxide reaction product was lost during the test and hence the oxidation state of the dissolved chromium was changed. If this conclusion is a proper one, the data suggest that equipment design

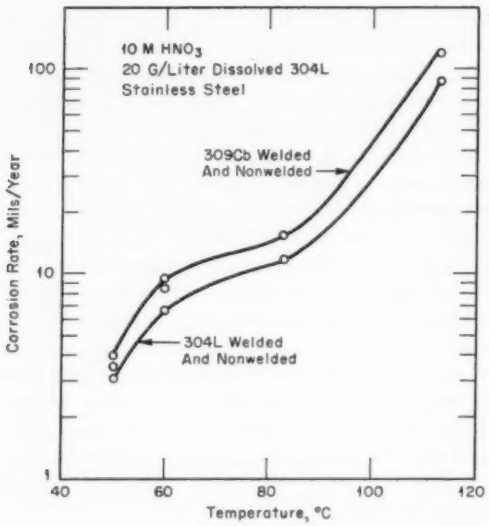

Fig. II-5 Effect of temperature on corrosion rate of stainless steels in nitric acid containing dissolved stainless steel.[20]

which would encourage retention of these noncondensables in the gas phase would be desirable.

Oak Ridge is considering the possibility of using a common centrifuge for a number of solutions resulting from head-end processing.[7,13,53] Since clarification of solutions by centrifugation can be done at room temperature, the corrosiveness of these solutions might be sufficiently low to make them compatible with a single construction material. Corrosion testing of five alloys in five process environments was begun. The five alloys were low carbon Nionel, Carpenter-20SCb, titanium-45A, Hastelloy C, and Hastelloy F. The five process solutions were Darex, Zirflex, Sulfex, Thorex, and uranium dioxide–core dissolvents, containing the dissolved constituents which would be present at completion. A partial listing of these results is shown in Table II-5. Low carbon Nionel and Carpenter-20SCb were severely corroded in the vapor phase and at the interface with Darex dissolvent. All five alloys had reasonable resistance to Zirflex, Sulfex, and final Thorex dissolvents. The best alloys for the uranium dioxide–core dissolvent (containing 0.05*M* sodium fluoride) were low carbon Nionel, Carpenter-20SCb, and Hastelloy F. The corrosion of titanium-45A and Hastelloy C in

Table II-5 CORROSION OF ALLOYS IN FIVE HEAD-END PROCESS SOLUTIONS FOR APPLICATION TO MULTIPURPOSE CENTRIFUGE[7,13,53]

(Temperature, 35°C; Exposure Time, 168 to 674 Hr)

Alloy	Corrosion rate, mils/month				
	Process solution*				
	Darex	Zirflex	Sulfex	Final Thorex	UO_2 core
LCNA†	>50‡	0.01	0.08	0.03	0.4
Carpenter-20SCb	>50‡	0.02	0.02	0.05	0.5
Titanium-45A	0.02	6§	0.04	<0.01	11¶
Hastelloy C	0.4	0.01	0.06	0.4	5¶
Hastelloy F	0.09	0.04	0.01	0.05	0.6

* Process solutions contained appropriate dissolved metal constituents.

† Low carbon Nionel alloy.

‡ Severe corrosion in vapor and at interface.

§ Corrosion rate decreasing with time.

¶ Test terminated because of severe attack at solution and interface positions.

this solution was sufficiently severe to terminate the test. The data suggest that Hastelloy F is the most promising material at the present time for multiple-purpose use for a process centrifuge.

Experiments to determine what alloy might be suitable for the evaporation of Purex waste solutions have been carried out at Oak Ridge.[7,53] Hastelloy F appeared to be only slightly sensitive to the presence of 0.002*M* ruthenium. The rates of attack were 2.8 and 1.9 mils/month with and without ruthenium, respectively. Stainless-steel type 347 suffered general surface corrosion of 3.6 mils/month, but severe grain-boundary attack limits its usefulness. Welded titanium-45A had negligible attack.

The condensate from the above evaporation varies in composition from 6*M* nitric acid–0.05*M* sulfuric acid to 15*M* nitric acid–1*M* sulfuric acid. Low carbon Nionel, Hastelloy F, and titanium-45A were exposed in refluxing condensate of both the high and low acid compositions.[7,13,53] In the low acid composition, both low carbon Nionel and Hastelloy F corroded at an increasing rate varying from about 0.05 mil/month after 168 hr to 2 and 3 mils/month after 672 hr. These numbers were similar to those obtained in parallel tests in which the refluxing condensate did not contain 0.05*M* sulfuric acid. Titanium-45A behaved well in both low and high acid environments, although some small amounts of localized attack in the

heat-affected zones near welds were observed in solution and interface specimens from the high acid environment. Generalized surface attack was 2 and 4 mils/month for exposure to the low and high acid condensate, respectively.

Development studies at the ICPP are directed at modifying its existing zirconium-alloy-fuel processing facility. One of the methods being explored is the head-end precipitation of zirconium and fluoride from the dissolver solution as barium fluozirconate. With a high percentage of the total solids removed, resulting waste solutions from solvent-extraction processing lend themselves to further volume reduction by evaporation. Such synthetic waste solutions were used in corrosion tests at 95°C with welded and unwelded Carpenter-20 and stainless-steel types 347 and 304L. The two solutions used in these preliminary tests were: (1) 4*M* nitric acid–0.1*M* barium fluozirconate and (2) 1*M* nitric acid–0.1*M* barium fluozirconate–0.4*M* barium fluoride. Surface corrosion on all these alloys varied from 6.5 up to 14 mils/month. The Carpenter-20 and type 347 stainless steel showed severe intergranular preferential weld-metal attack. Additions of aluminum could be made to complex residual free fluoride; however, this can be done only at the expense of increasing the total solids content.[25]

The ICPP has completed a study of the corrosiveness of nine different decontaminating solutions on five alloys used in its plants.[54] The solutions and alloys together with partial results are shown in Table II-6. All the alloys exhibited suitable corrosion resistance to boiling solutions of 10 per cent citric acid, and all except Monel were resistant to boiling 10 per cent nitric acid. Titanium is unsuited for handling 10 per cent sodium hydroxide–2.5 per cent tartaric acid, but the other alloys appear to be acceptable. Considerable corrosion attack was observed on all alloys when immersed in 3 per cent sodium fluoride–20 per cent nitric acid. The material least attacked at the temperature of the test (144°F) appeared to be tantalum. Austenitic stainless steel exhibited relatively good resistance to boiling 10 per cent oxalic acid, whereas both Monel and titanium-55A were severely attacked. Boiling dilute solutions of periodic acid–nitric acid mixture and phosphoric acid attacked Monel and, to a lesser degree, titanium-55A. Boiling Turco 4501 dissolved tantalum. The data on which these findings are based were obtained after exposures of 24, 72, 168, and 360 hr.

The data from 14 of the most corrosive systems were fitted to the parabolic rate law. The resulting best curves on log-log plots are reproduced in the report.[54] The slopes of these curves vary from a low value of 0.30 to 0.72 (with one single value of 0.95). This infers, and properly so, that the corrosion rate of each of these 14 most aggressive systems decreases with time. This also suggests, however, that the corrosion rates listed in Table II-6 are likely to be more conservative than the values ob-

Table II-6 CORROSION OF DECONTAMINATION REAGENTS IN ALLOYS USED AT ICPP[54]

(Temperature, Boiling Point at 650 mm Hg; Exposure Time, 360 Hr)

Solution	Corrosion, mils/month				
	Carpenter-20	S.S. 347	Monel	Titanium	Tantalum
10% nitric acid	<0.1	<0.1	>300	<0.1	<0.1
10% citric acid	<0.1	<0.1	6	<0.1	<0.1
10% NaOH–25% tartaric acid	<0.1	<0.1	0.4	1*	<0.1
10% oxalic acid	0.3	3	24	30	<0.1
0.003*M* periodic acid–0.05*M* nitric acid	<0.1	<0.1	4	<0.1	<0.1
3% sodium fluoride–20% nitric acid†	4	7	130	50	3
Turco 4501	<0.1	0.2	0.2	20	200
Turco 4502	<0.1	<0.1	0.3	0.2	
0.25*M* phosphoric acid	<0.1	<0.1	30	6	<0.1

* Sample pitted to depth of 20 mils. † Test temperature for this reagent was 144°F.

tained in the first several hours of an actual decontamination. It is therefore necessary to use some caution in the interpretation of the data for short exposure periods.

Aqueous Homogeneous Reactor Processing

In homogeneous reactors the fissionable fuel is carried either in solution or as a slurry in a heat-transfer medium. Such reactors have the potential advantage of removing a side stream for either continuous or intermittent processing. On occasion, particularly with a test or prototype reactor, it becomes necessary to process the entire fuel inventory. This is being done with the Homogeneous Reactor Test at Oak Ridge. It was recently shut down in order to make repairs on the core vessel, which had been perforated at two locations in prior high-power operation. Eight kilograms of uranium contained in the fuel batch is to be processed for uranium decontamination and recovery.

Laboratory experiments are being performed to determine the best possible technique for the operation.[55] Laboratory tests of the peroxide precipitation method had been performed on synthetic nonradioactive solutions. Difficulty was encountered in retaining the peroxide precipitate on a stainless-steel filter of G pore size. The use of filter aids improved retention; however, the precipitate was not contained at pressure differences greater than about 15 psi across the filter.

An alternate procedure involving ion exchange is also being investigated. The use of anion-exchange resin Dowex 1 appears to be the most promising. When a synthetic solution of the composition in the decay tanks was diluted by a factor of 15 and partially neutralized with ammonium hydroxide, a resin loading of 30 g/liter could be obtained with a loss of only 0.03 per cent. The uranium could be eluted successfully with 1*N* nitric acid and precipitated as a peroxide from the solution. Filtration of this resulting precipitate is not discussed in the report.

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Section III

RESEARCH AND DEVELOPMENT ON NONAQUEOUS PROCESSING

Nonaqueous processes under development for separating valuable materials from used reactor fuels include volatility processes based on both fluoride and chloride systems, pyrometallurgical and other high-temperature processes, and certain electrolytic processes. Some of these methods are being considered as head-end operations for solvent-extraction processes, but most are complete processes of either the high- or low-decontamination type. The latter type is designed to be used in conjunction with remote fuel refabrication techniques. None of the nonaqueous methods are yet in use in processing plants, but the construction of a pyrometallurgical process facility for the second Experimental Breeder Reactor (EBR-II) is nearly completed.

Volatility Processes

The volatilities of uranium and plutonium hexafluorides have been proposed as a basis for processing various types of irradiated nuclear reactor fuels. Liquid-phase fused-salt processes are being considered for application to the recovery of uranium from molten-salt reactor fuel and from zirconium-uranium alloy fuel. Solid phase–gas phase halogenation processes have also been proposed for application to zirconium-uranium alloy fuel and to uranium dioxide fuels. Fluidization techniques are employed in some of these dry halogenation processes to enhance process control. In this review, results are summarized for laboratory-scale dissolution of reactor fuels in liquid NO_2-HF, engineering corrosion experience in handling fused chloride salts, developments in the Zircex process, and physical properties of volatile and nonvolatile fluoride compounds of process interest.

Liquid-Phase Processing

Dissolution of Fuel Materials in NO_2-HF. The initial step in the Nitrofluor process (flow sheet given in a previous Review[1]), under development at Brookhaven National Laboratory, involves the dissolution of the reactor fuel assembly in an anhydrous nitrogen dioxide–hydrogen fluoride solution. A solution containing 25 mole % nitrogen dioxide is capable of dissolving a wide variety of fuel-element materials at satisfactory rates over a temperature range of 100 to 200°C. The flow sheet proposed for enriched uranium–zirconium alloy fuel consists of dissolution in the solvent, separation of the insoluble zirconium salt from the soluble uranium salt, evaporation of the uranium-containing solution, fluorination of the residue with bromine trifluoride, and purification of the uranium hexafluoride formed, by distillation. Variations of the process are necessary for low-enrichment fuels, since the quantity of uranium involved is considerably increased, and the recovery of plutonium must be considered.

The processing of enriched uranium–zirconium alloy fuels involves the separation of the complex zirconium and uranium salts based on solubility. Although the salt solubilities are comparable, the high zirconium–uranium ratio results in precipitation of nearly all the zirconium salt. Experiments[2] have been performed to determine the feasibility of eliminating the process step involving separating the uranium from the insoluble zirconium salt prior to fluorination. The dissolver solution was dried at 150°C to decompose the complex salts to the normal fluorides. After three contacts with bromine trifluoride at 121°C, only 82 per cent of the uranium content was recovered as uranium hexafluoride. The remainder of the uranium remained in the zirconium tetrafluoride salt.

Further work is suggested to improve the recovery of uranium by selective fluorination with bromine trifluoride from systems containing zirconium tetrafluoride.

The complex plutonium salt is soluble in the nitrogen dioxide–hydrogen fluoride solvent. Studies have been undertaken to observe the conversion of plutonium and uranium salts to volatile hexafluorides with fluorine gas in the absence and presence of the complex zirconium salt.[2] The dissolution, evaporation, and fluorination steps were performed starting with a uranium-plutonium alloy containing 0.056 per cent plutonium. Without zirconium present, 88 per cent of the plutonium and 99.5 per cent of the uranium were volatile after fluorination for 6.5 hr at 375°C. In the presence of approximately 20 per cent zirconium tetrafluoride, essentially all the uranium but only 15 per cent of the plutonium was volatile. It was concluded that most of the plutonium tetrafluoride was not contacted with fluorine due to occlusion by the zirconium tetrafluoride particles during evaporation of the solvent.

A reactor fuel containing 3.5 per cent uranium monocarbide in graphite was evaluated[2] for dissolution in the nitrogen dioxide–hydrogen fluoride solvent. A cube of this material was disintegrated in a 17 mole % nitrogen dioxide–83 mole % hydrogen fluoride solution for 4 hr at 193°C. Approximately 89 per cent of the uranium was extracted by the solvent. Repeated contacts on the graphite residue with fresh solvent recovered essentially all the remaining uranium.

Sintered thorium dioxide–uranium dioxide fuel material does not react with the Nitrofluor solvent.[3] A variety of solvents are being evaluated as a dissolution medium; but no promising results have been obtained thus far.[2]

Freezing-point data have been obtained[2] for the nitrogen dioxide–hydrogen fluoride system in an attempt to determine the reactive species present in the solvent. The data presented in Fig. III-1 indicate a eutectic point at 10 mole % nitrogen dioxide (–144°C). An incongruent point was observed at 20 mole % nitrogen dioxide (–52°C). This point could indicate a maximum at 25 mole % nitrogen dioxide hidden by the higher freezing point compound at 30 mole % nitrogen dioxide (–26°C). Above 44 mole % nitrogen dioxide, the liquid separates into two phases at room temperature,

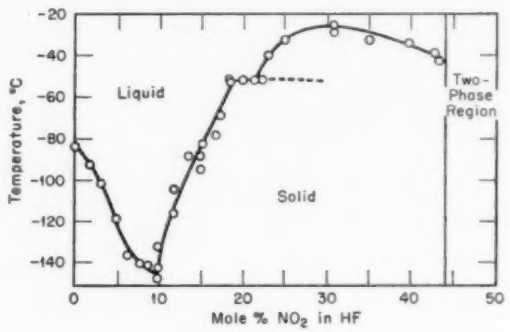

Fig. III-1 Freezing points of nitrogen dioxide–hydrogen fluoride mixtures.

and miscibility does not occur at temperatures as high as 80°C.

Corrosion in the Fluorination Step of the Fused-Salt Process. In the fused-salt fluoride-volatility process, uranium hexafluoride is formed and separated by sparging a molten fluoride salt with fluorine. This process step has been shown to be rapid and complete, but serious corrosion has been exhibited in long-term operation. A critical summary of corrosion in this process has been published, in which ORNL pilot-plant and small-scale fluorinator corrosion data are evaluated.[4]

Satisfactory container materials are available for fluorine gas alone up to about 600°C and also for molten fluorides in the absence of fluorine, but the combination process environment presents a more difficult corrosion problem. Although the fluorides formed on the surface of metals can be highly protective in a fluorinating environment, they are dissolved away by molten salt. Even for the parts of the fluorinator not in direct contact with the molten salt, the effectiveness of protective films has been lowered by condensable or specially reactive vapor components above the high-temperature salt. Detailed analysis and careful correlation of extensive corrosion data by Litman and others at ORNL has confirmed some basic effects, discounted certain suspected corrosion mechanisms, and explained some previously anomalous results.

The data were obtained from the operation of two pilot-plant fluorinators and three different types of smaller, bench-scale fluorinators. The pilot-plant units were used for processing Aircraft Reactor Experiment (ARE) fuel (cited in

the January 1959 issue of *Reactor Fuel Processing*, page 20) and also were used to expose numerous corrosion specimens of various alloys to the processing environment; this includes vapor, interface, and salt zones for each specimen. The bench-scale units were used for both process and corrosion studies. Major emphasis was put on metallurgical analysis of the exposed metal.

Table III-1 SUMMARY OF CORROSION RESULTS IN FUSED-SALT FLUORINATORS[4]

Fluorinator	Temp., °C	Uranium	Maximum observed total corrosion rate: Based on salt exposure,* mils/month	Maximum observed total corrosion rate: Fluorine-salt exposure, mils/hr	Zone of maximum attack
Pilot plant, Mark-II (L-nickel)	540–730	Yes	60	1.1	Salt
Bench-scale (Inconel)	600–800	Yes	48	0.24	Interface
Bench-scale (A-nickel)	600	Yes	38	0.3	Interface
	600	No	16	0.12	Interface
	525	No	5–20	0.3–0.12	Interface
	450	No	3	0.02	Interface
Bench-scale (INOR-8)	600	No	30	0.28	Interface
	450	No	5	0.04	Interface
	450	Yes	13	0.12	Interface

*The salt was sparged with fluorine for only a fraction of the total salt-exposure time.

Maximum corrosion rates observed in these different types of fluorinators are shown in Table III-1. In spite of differences in configuration, in alloys, in salt compositions, and in processing conditions, considerable agreement is shown. These data indicate higher attack at higher temperatures and with increased fluorinating potential in the salt phase. Higher fluorination attack in the molten-salt region accompanies the alternate fluorine-salt exposure at the interface and higher concentrations of uranium fluorides in the salt phase.

The alloys in Table III-1 are all high nickel, and the superiority of high nickel alloys has been confirmed in examination of corrosion specimens. The alloy specimens showing best resistance to the pilot-plant environment are shown in Table III-2. The corrosion rates in Tables III-1 and III-2 are for total attack (both metal loss and intergranular penetration) and for the regions of maximum attack. The compositions of these alloys are listed in Table III-3.

Table III-2 CORROSION OF ALLOY SPECIMENS EXPOSED IN ORNL PILOT-PLANT FLUORINATORS[4]

(Process Runs at 550 to 700°C; Selection of the Eight Specimens Least Attacked)

Alloy	Rate of metal loss: Based on salt exposure, mils/month	Rate of metal loss: Based on salt–fluorine exposure, mils/hr
Hymu 80	11	0.2
INOR-8	19	0.5
Waspalloy	19	0.5
INOR-2	22	0.4
Hastelloy W	24	0.6
L-nickel	27 (min.)*	0.7 (min.)*
Hastelloy X	31	0.7
90 Ni–10 Co	38	0.7

*L-nickel was the only material examined in multiple; the L-nickel sample with lowest corrosion is shown above. Other L-nickel samples showed several times these minimum values.

Certain metallurgical aspects suspected of contributing to corrosion in this application were not found significant after careful examination. These were sulfur embrittlement, carbide precipitation, and grain growth in nickel. However, the conditions for these known deleterious effects has been deliberately minimized in advance, and such an approach is still highly recommended.

Certain anomalous effects have been resolved. Very high vapor-phase attack has been attributed

to condensation of corrosive liquids by excessive cooling of the top of the vessel. Very low interface attack appeared due to a frozen salt crust due to the same condition. However, intergranular attack is not yet understood.

The general approach being continued at ORNL is the optimization of process conditions as far as possible (especially temperature reduction) and the search for more resistant alloys. From the results of Table III-2, it appears that some improvement can be expected over the results obtained with L-nickel. A similar report for the hydrofluorination step in fused-salt processing is in preparation.

Dry Halogenation Processes

Several processes which involve separation methods based on the relative volatility of the chlorides are being developed for processing of reactor fuel elements. In the Zircex process,[5,6] developed at ORNL, uranium is sepa-

Table III-3 NOMINAL COMPOSITION OF CORROSION SPECIMENS FROM THE VOLATILITY PILOT-PLANT FLUORINATOR[4]

Material	Nominal composition, wt.%														
	Ni	Fe	Co	Al	Mn	Ti	Mo	Cr	C	W	V	Zr	S	Si	P
L-nickel	99.47	0.11			0.17				0.023				0.0075	<0.01	
Hymu 80	79	16 (bal.)			0.50		4.0		0.05					0.15	
90 Ni–10 Co	90.02	9.63	9.63						0.020						
Hastelloy X	48 (bal.)	18.76	1.01		0.64		8.82	21.81	0.11	0.20			0.008	0.78	0.011
Waspalloy	57 (bal.)	2 (max.)	12–15	1–1.5	0.5 (max.)	2.75–3.25	3.5–5	18–21	0.1 (max.)			0.1	0.03 (max.)	0.75 (max.)	
Hastelloy W	60	5.5	2.5		1		25	5	0.12		0.6				
INOR-2	79						16	5	0.1						
INOR-8	69.8	5.1			0.83	0.08	16.5	6.9	0.08				0.005	0.14	0.008

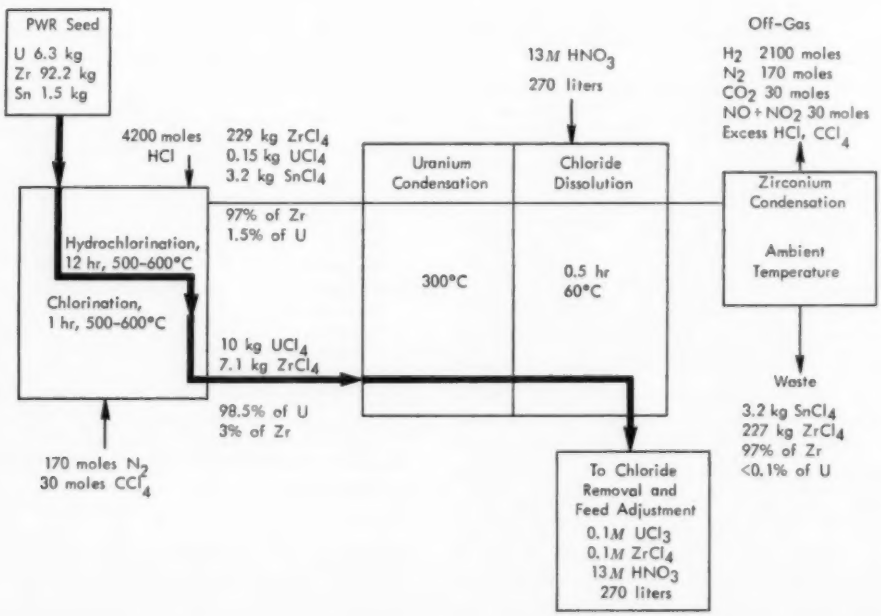

Fig. III-2 Modified Zircex process: gas-phase hydrochlorination of PWR seed followed by chlorination with carbon tetrachloride.

rated from zirconium by volatilization of zirconium tetrachloride and finally recovered by solvent-extraction techniques. The Zircex process has been extended in laboratory studies to include both niobium and molybdenum alloys of uranium.[6,7] A process based on the selective chlorination of uranium to produce volatile uranium hexachloride has been studied.[8,9]

The Zircex process is based on the use of hydrogen chloride, at a fuel-element temperature of 600°C, to convert the zirconium-uranium alloy to volatile zirconium tetrachloride and nonvolatile uranium trichloride. A flow sheet[4] based on the processing of the Shippingport PWR seed (6.3 per cent uranium–93.7 per cent Zircaloy) is shown in Fig. III-2. About 1 to 10 per cent of the uranium volatilizes at 600°C during the hydrochlorination, depending on the alloy composition, and is transported with the zirconium tetrachloride from the reactor. This uranium is collected in a condenser operating at 300°C. Zirconium tetrachloride, which has a vapor pressure of 0.3 atm, passes through the 300°C condenser and is collected in a separate condenser at room temperature. Owing to the presence of oxygen-containing impurities, introduced with the hydrogen chloride or dissolved in the fuel alloy, about 3 per cent of the zirconium remains in the uranium product as nonvolatile zirconium oxide or oxychloride. The nonvolatile hydrochlorination product is converted to volatile chlorides by chlorination at 500 to 600°C with carbon tetrachloride diluted with nitrogen. Owing to the reaction involving the oxidation of U(III) to U(IV) with carbon tetrachloride, some carbon is deposited in the reactor, and therefore a brief burnoff with air is needed during the chlorination step. The uranium chloride (primarily uranium tetrachloride) gas is selectively condensed at 300°C. A uranium loss of less than 0.1 per cent occurs by passage of some uranium chloride through the condenser. Various schemes were tried to effect complete condensation in the uranium condenser: baffles, 5-μ porous metal filters, and screens were evaluated, but none of these was as effective as a dense packing of metal wool for reducing uranium losses. The uranium is removed from the condenser by dissolution in water or nitric acid. A chloride-free (100 ppm) solvent-extraction feed can be prepared by dissolving the uranium chloride condensate in 13*N* nitric acid and distilling the chloride from the solution.

The possibility of recovering the uranium from the chloride condenser directly as uranium hexafluoride has been demonstrated in a single laboratory-scale experiment by fluorinating with fluorine[6] at 200°C. In view of the high uranium recovery (98 per cent), further work is planned in larger scale equipment.

The Zircex flow sheet has been extended in preliminary investigations to include other reactor materials. The reaction rate of niobium with hydrogen chloride and chlorine to produce niobium pentachloride has been measured.[6] The formation of a protective oxide coating on the metal surface which tends to inhibit reaction with hydrogen chloride can be prevented by saturating the hydrogen chloride gas with carbon tetrachloride at 25°C. Preliminary studies[7] have been made on the reaction between type 304 stainless steel and chlorine at 600°C.

The reaction between zirconium metal and hydrogen chloride gas is highly exothermic, and a major problem associated with the Zircex process is the removal of heat generated in the reaction. At Brookhaven National Laboratory[2,3] a fluidized bed of inert particles is used to provide rapid and efficient heat transfer from the reaction zone. The volatile zirconium tetrachloride is transported from the fluid-bed reactor and is either condensed or recovered as zirconium oxide by pyrohydrolysis with steam. The uranium trichloride residue is reacted with fluorine to recover the uranium as the hexafluoride. A summary of the laboratory and pilot-plant development work on the process has been published recently.[10] It was demonstrated in a 6-in.-diameter fluid-bed reactor that a large multiplate fuel element could be hydrochlorinated without any difficulty with respect to temperature control. Uranium losses through entrainment or volatilization were less than 1 per cent. The fluorination recovery has been investigated only in small-scale laboratory experiments. Preliminary results indicate that extended fluorination periods will not result in complete uranium removal from the inert-bed material. This might necessitate recycle of the inert bed through several hydrochlorination-fluorination cycles in order to achieve an overall uranium recovery of 99 per cent.

Scouting tests have also been made on the fluid-bed chlorination of stainless steel and fluorination of uranium metal.[2,10] Due to the high temperature (approximately 650°C) nec-

essary to achieve practical reaction rates between chlorine and stainless steel, corrosion of the reactor vessel becomes a serious problem. Although a fluidized bed is a good heat conductor, the same bed in a settled state may be considered a good heat insulator, and it should be possible to establish a condition wherein the major portion of the settled bed is held at a much higher temperature than the container vessel. Therefore the possibility of using a static bed to insulate the vessel wall from the reaction zone was investigated. In a single test it was possible to maintain the wall temperature between 480 and 510°C while the chlorination reaction temperature was approximately 640°C.

An oxyhydrochlorination process flow sheet, based on laboratory-scale data,[7] has been developed for preparing uranium-molybdenum alloys [Consumers Public Power District (CPPD) of molybdenum and chloride, and oxide dissolution in nitric acid. It was proposed that the original stainless-steel cladding would be mechanically removed and the fuel recanned in aluminum prior to the core processing. The CPPD fuel, canned in 32-mil aluminum, is treated for 2 hr at 300°C with 60 per cent hydrogen chloride in nitrogen to remove the can as volatile aluminum chloride (Al_2Cl_6). Approximately 1 per cent of the aluminum remains with the core as oxide due to reaction with oxygen-containing impurities. Oxidation of the core is achieved by the reaction with 15 vol.% hydrogen chloride in air at 400°C. The reaction products are a volatile molybdenum oxychloride (MoO_2Cl_2) and nonvolatile uranosic oxide (U_3O_8). An 18-hr treatment is sufficient to complete the oxidation and to volatilize 90 per cent of the molybdenum. However, additional treatment is necessary to remove part

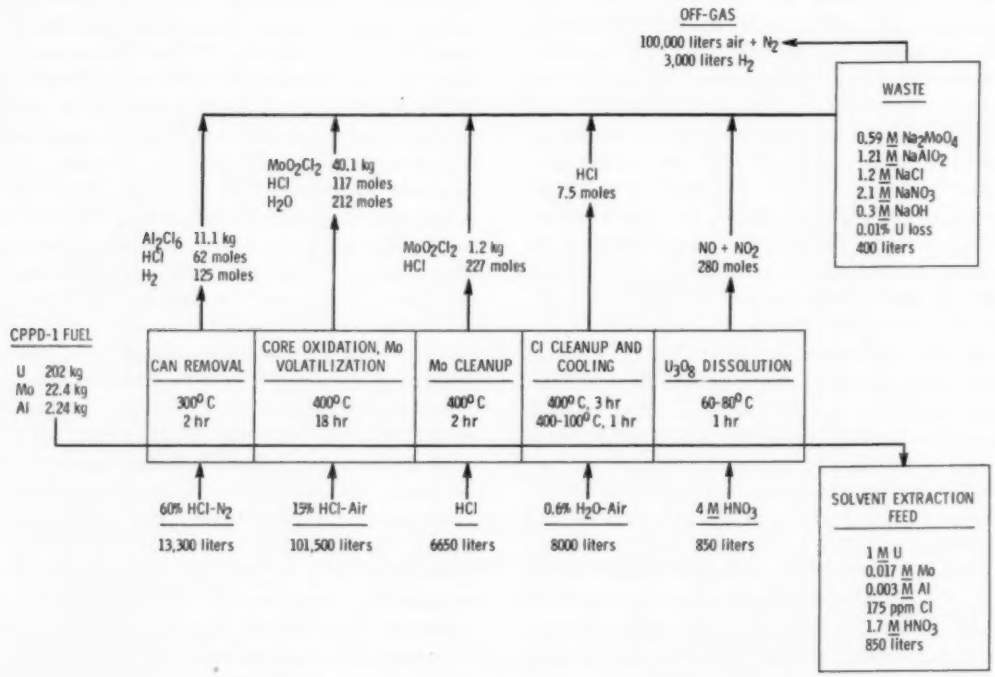

Fig. III-3 Oxyhydrochlorination flow sheet for removal of aluminum can and processing of CPPD fuel.

core, 90 per cent uranium–10 per cent molybdenum] for solvent extraction. The flow sheet (Fig. III-3) involves five operations: can removal, core oxidation, purification by removal of the residual molybdenum and chloride before a satisfactory solvent-extraction feed solution can be prepared by dissolution in nitric acid. Treatment of the residue with hydrogen chlo-

ride at 400°C for 2 hr removes an additional 3 per cent of the molybdenum, which is sufficient to ensure stability of the solvent-extraction feed solution. A 4-hr treatment with 0.6 per cent water vapor in air at 400°C removes more than half of the remaining chloride. The U_3O_8 product dissolves readily in 4*M* nitric acid to yield a stable solution of 1*M* uranium, 0.017*M* molybdenum, 0.003*M* aluminum, 175 ppm chloride, and 1.7*M* nitric acid. This proposed high-temperature process is said to produce a smaller high-level radioactive waste volume than the aqueous dissolution process. Also, the solids separation step, used in the aqueous dissolution to separate the insoluble molybdenum oxide particles from the uranium solution, is avoided.

The decontamination of irradiated uranium by the fractional sublimation of chlorides is being studied[8,9] at Centre d'Étude de l'Énergie Nucléaire, Brussels. The method is based on the fact that the vapor pressures of uranium chlorides increase with valence.

Decontamination takes place in five steps:

1. The uranium alloy is treated in a stream of hydrogen at 250°C to form the hydrides.

2. The hydride, or the alloy when some of it does not react in step 1, is heated to 250°C in the presence of dry hydrogen chloride. The products formed depend on the uranium alloy being processed. Alloys containing aluminum or zirconium react to produce volatile chlorides in addition to nonvolatile uranium trichloride, whereas alloys of molybdenum or niobium do not react. The volatile aluminum, zirconium, and fission-product chlorides are removed by heating at 250°C under vacuum.

3. The uranium trichloride is treated at 150°C in a chlorine-gas stream to produce uranium tetrachloride. The chlorides of molybdenum and niobium are removed.

4. Uranium hexachloride is produced by reaction of uranium tetrachloride with chlorine at 400°C. The volatile chloride is transported from the reaction vessel and collected in a condenser. The presence of small quantities of oxygen within the system may contribute to the formation of a nonvolatile residue of uranium oxychloride ($UOCl_2$).

5. The uranium hexachloride is resublimed at 160°C under reduced pressure in a stream of chlorine as a final purification step.

This process sequence has been evaluated[9] with irradiated (integrated flux of 10^{17} neutrons/cm^2) uranium alloys of aluminum, zirconium, molybdenum, and niobium. A 99 per cent chemical separation was obtained for aluminum and zirconium. However, the separations of molybdenum and niobium from uranium were much lower. The yield of sublimed uranium was low because of partial oxidation during the final chlorination step. The decontamination factor was 100 for beta activity, but less for gamma activity. The fission products most difficult to remove were Zr^{95} and Nb^{95}. The second sublimation purification step was useful in removing Ce^{141}, Ru^{103}, and La^{140} but did not effect any decontamination of either zirconium or niobium.

Physical and Chemical Properties of Fluorides

Adsorption of Volatile Fluorides on Solids. Uranium hexafluoride, as produced in several proposed fluoride-volatility processes, will be contaminated with both volatile fission-product and corrosion-product fluorides. One method under investigation for the purification of uranium hexafluoride is by sorption-desorption through a bed of sodium fluoride. The kinetics of adsorption and desorption of uranium hexafluoride and other volatile metal fluorides by sodium fluoride have been measured by Krause and Potts.[11] The maximum adsorption rate for uranium hexafluoride was obtained at 100°C. Sorption rate varied directly with the concentration of uranium hexafluoride in the gas phase and inversely with temperature. Nitrogen and fluoride carrier gases were essentially equivalent in their effect on adsorption. Desorption of uranium hexafluoride was extremely fast at 400°C. Approximately 2 to 5 per cent of the uranium remained deposited on the bed, and this deposition appeared to be cumulative in successive adsorption-desorption cycles. The sorption capacity of the sodium fluoride is appreciably reduced after the initial cycle. However, the sorption capacity is stabilized at the lower value in subsequent cycles.

Other fluorides (silicon tetrafluoride, molybdenum hexafluoride, ruthenium pentafluoride, tellurium hexafluoride, and iodine pentafluoride) were examined[11] briefly to determine the optimum sorption range. Of these fluorides, only molybdenum hexafluoride gave appreciable adsorption in the optimum uranium hexafluoride

temperature range (100°C). Rapid desorption of molybdenum hexafluoride from the sodium fluoride bed occurs at 300 to 400°C. A basis for separation of molybdenum and uranium hexafluoride may exist at a temperature of 200°C where adsorption is appreciable for uranium but not for molybdenum hexafluoride. Optimum sorption for silicon tetrafluoride occurs at 300°C, and desorption does not occur at a rapid rate below 600°C. Appreciable adsorption of ruthenium pentafluoride occurs at 400°C. Iodine pentafluoride and tellurium hexafluoride gave very little sorption (less than 5 per cent) at 100 to 300°C.

The dissociation pressure of the complex formed when molybdenum hexafluoride is adsorbed on sodium fluoride has been measured at 100 and 150°C at ORNL.[12] The lower and upper limits were 0.4 to 4.6 mm Hg at 100°C and 8.4 to 27 mm Hg at 150°C. Similar measurements were made at 150°C with niobium pentafluoride.[12]

Preparation and Properties of Volatile Fluorides and Oxyfluorides. Cady and Hargreaves[13,14] have published their data on the vapor pressures of the fluorides and oxyfluorides of several heavy transition metals. Some of the physical and thermodynamic constants derived from these vapor-pressure data were reported in a previous Review.[1] In this study[13] it was observed from nuclear magnetic resonance spectra that there is molecular rotation in the solid state of some hexafluorides at temperatures above the solid-solid transition point. Molecular rotation and molecular distortion in the condensed phases may have a significant effect on the equilibrium thermodynamic properties of these compounds, as pointed out by Weinstock.[15] An illustration of the fact that molecular distortion affects the vapor pressure of uranium hexafluoride is the large positive deviations from Raoult's law observed in fluorocarbon solutions of the fluoride.[15]

Ruthenium hexafluoride has been prepared at Argonne National Laboratory by heating ruthenium metal powder in a fluorine atmosphere at 300 mm Hg pressure.[16,17] Once initiated, the reaction proceeded without further heating. The volatile reaction products were condensed rapidly by keeping the walls of the reactor and a cold finger at liquid-nitrogen temperature. Preliminary vapor-pressure measurements indicate that ruthenium hexafluoride is the least volatile of the three known 4d transition series hexafluorides (MoF_6 and TcF_6). The dark-brown solid has a transformation point at 2.5°C and melts at 54°C.

The preparation of rhenium hexafluoride by the reaction of chlorine trifluoride gas on the metal at 300°C has been reported.[18] Liquid chlorine trifluoride has little effect on powdered rhenium metal. The preparation of the hexafluoride by reaction of powdered metal, pretreated with hydrogen, with fluorine is described by Cady and Hargreaves.[13]

The reaction between uranyl fluoride and chlorine trifluoride to produce uranium hexafluoride has been studied[19] in the temperature range 50 to 150°C. The reaction proceeds to completion in the temperature range studied with the gaseous reaction products being, in addition to uranium hexafluoride, oxygen, chlorine, chlorine monofluoride, and chlorylfluoride. Chlorine dioxide may be present as a reaction intermediate. At 150°C the stoichiometry of the reaction may be expressed by

$$2UO_2F_2 + 4ClF_3 \rightarrow 2UF_6 + Cl_2 + ClF + ClO_2F + O_2 + F_2$$

The initial reaction of residual water of hydration in uranyl fluoride with chlorine trifluoride is very rapid compared with the subsequent process producing uranium hexafluoride.

The reactions of uranium, molybdenum, and tungsten hexafluoride with nitrogen dioxide and nitrogen oxyhalides have been studied at the Goodyear Atomic Corporation,[20] and several of the product compounds have been characterized. With gaseous nitrogen dioxide, uranium hexafluoride reacts to form nitrylium hexafluorouranate (V), NO_2UF_6, a yellow-white solid having no vapor pressure at 25°C. No reaction was observed between nitrogen dioxide and molybdenum or tungsten hexafluoride. All three hexafluorides were found to form 1:1 addition compounds with both nitrosyl and nitryl fluorides as $NO_xF(g) + MF_6(g) = NO_xF \cdot MF_6(s)$, where x has the value of 1 or 2, and M represents molybdenum, tungsten, or uranium. Reaction between gaseous or liquid nitrosyl chloride and molybdenum and uranium hexafluorides results in the formation of the nitrosylium salts, $NOMoF_6$ and $NOUF_6$, and chlorine. Tungsten hexafluoride was found not to react with nitrosyl chloride.

X-ray-diffraction data and physical properties such as color, stoichiometry, and density are reported for nine new compounds, six of which are reaction products of nitrogen oxides with hexafluorides and three of which are reaction products of uranium hexafluoride with various cations. The compounds are $NOUF_6$, $NOMoF_6$, $NOMoOF_5$, $NOWOF_5$, NO_2UF_6, NO_2UF_7, $Ca(UF_6)_2$, KUF_6, and $LiUF_6$. The reaction conditions giving these products are also listed.[21]

A table listing the temperature-dependent coefficients for the computation of thermodynamic properties of gaseous uranium hexafluoride has been prepared[22] from equations that express the properties as expansions in powers of pressure. The coefficients listed have been computed in 1° increments for a temperature range of 500 to 999°R.

The Chemistry and Separation of Plutonium Hexafluoride and Uranium Hexafluoride. Plutonium hexafluoride has acquired a well-deserved reputation for instability. It is a highly reactive material and therefore must be prepared under carefully controlled conditions. The ease of decomposition can, however, be an advantage in separating it from uranium hexafluoride. Experiments have been performed at ANL[23] on the fluorination of multigram quantities of plutonium dioxide, in which 97 to 99 per cent of the plutonium was accounted for in the volatile effluent. Experiments have been made to demonstrate that plutonium hexafluoride produced in a laboratory fluorinator can be passed through heated sections of pipe and through thermal gradients with very good recovery of the compound. Trap-to-trap transport through laboratory equipment has demonstrated that 98 to 100 per cent of the plutonium hexafluoride volatilized could be recovered. It has also been demonstrated[23] that a 38-g sample of plutonium hexafluoride could be held at 60°C for 25.5 hr with no more decomposition than could be attributed to alpha-radiation decomposition.[23]

Trevorrow and others[24] at ANL have reported stoichiometric and equilibrium determinations of the thermal decomposition reaction of plutonium hexafluoride at temperatures from 150 to 400°C. The reaction products under these conditions were gaseous fluorine and solid plutonium tetrafluoride. Below 300°C the equilibrium constants (moles PuF_2/moles F_2) were found to be higher than literature values. The sharp change in the relation between log K and $1/T$ at 308°C reported previously was not found in the present work. The relation between equilibrium constant and temperature is expressed by the equation $\log K = -1331/T(°K) - 0.275$.

The reaction of bromine with plutonium hexafluoride, with and without the presence of uranium hexafluoride, has been investigated.[23] Bromine is a satisfactory reagent for the reduction of plutonium hexafluoride to plutonium tetrafluoride and can be used to separate uranium and plutonium.

The gamma-ray spectrum of plutonium tetrafluoride has been investigated up to 2.0 Mev. Fast-neutron-flux measurements have been made on samples of plutonium tetrafluoride to assay the hazards connected with the (α,n) reaction which occurs by nuclear interaction between the alpha particles emitted by plutonium and the fluorine atom.[23]

Pyrometallurgical Processing

In the pyrometallurgical processes under development, potential reductions in processing costs result mainly from general process features such as simplicity, compactness, avoidance of chemical conversions, and capability of handling short-cooled fuels with an attendant reduction in fuel inventories. In some processes the fuel is retained in the metallic state, whereas in others momentary departures from the metallic state are utilized to achieve separation from impurities. An example of the latter is a procedure involving oxidation-reduction reactions conducted in the presence of fused-salt and molten-metal phases either by electrolysis or by the use of chemical oxidants and reductants.

Melt Refining

As the first process to be tested in the fuel-cycle facility being built adjacent to the EBR-II for recovery and recycle of discharged fuel from this reactor, melt refining is receiving[25] considerable attention in the pyrometallurgical processing field. This relatively simple process consists of melting the discharged uranium-fissium alloy fuel in a calcium oxide–stabilized zirconia crucible and holding it at a temperature of 1400°C for several hours to effect fission-product removal by volatilization and by selective oxidation reactions.

As of June 1, 1961, construction of the fuel-cycle facility was over 90 per cent complete. Installation of in-cell crane and manipulator bridges has been completed. Installation of the 5-ft-thick glass shielding windows is under way, the design of which (see Fig. III-4) has been

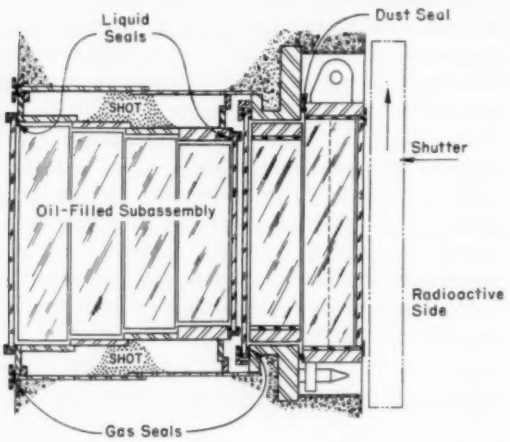

Fig. III-4 Shielding window for EBR-II fuel-cycle facility.[26]

patented.[26] Most of the processing equipment is now being fabricated. A record of progress in this area is provided by quarterly reports of the Argonne Chemical Engineering Division, the latest being ANL-6379 [25]

Minor cracking of the plant-size calcia-stabilized zirconia crucibles used for melt refining has sometimes occurred. Although difficulties resulting from metal leakage have been rare, the cracking has created some concern. The problem has been alleviated[25] considerably by (1) visual inspection of crucibles and rejection of those with initial cracks and extremely large grains, (2) reduction of thermal shock during heatup by a gradual application of power, and (3) making the thickness of the crucible bottom equal to that of the side wall.

Outgassing studies on a sample of a plant type zirconia crucible showed that only a small amount of gas (2.5 cm^3 per 100 g) was removed by heating to 1100°C under vacuum.[25] The major gases removed were water vapor and carbon dioxide, with smaller amounts of oxygen, nitrogen, argon, and possibly hydrogen. A furnace for outgassing plant crucibles is being provided at the fuel-cycle facility, not only to outgas crucibles but also to provide a test of the crucibles prior to use.

Of possible interest to the melt-refining process are thermal diffusivity measurements made by Flieger et al.[27] on dense polycrystalline zirconium oxide which had been stabilized with magnesium oxide. The data show the stabilization to be inadequate since the thermal diffusivity progressively increased after thermal cycling to about 1200°C. The increase is attributed to a gradual change from the cubic to the monoclinic crystalline form.[27]

The pattern of release of the fission gases, xenon and krypton, from highly irradiated EBR-II fuel material during melt refining has previously been reported in these Reviews.[28] Study of the evolution of these gases has been concluded at Argonne and may be summarized as follows. The rate of gas release is relatively low below 749°C, with an apparent activation energy of 3.6 kcal/mole. Above 749°C the rate rises sharply. At 850°C the quantity of xenon released in 2 hr was about 7000 times that at 749°C.

Significant quantities of volatile fission products are also released during melt refining. In high-activity-level experiments at Argonne, the principal one of these has been found to be I^{131}. Barium-140, La^{140}, and Cs^{137} have been found in smaller amounts.

The noble fission-product elements such as ruthenium, rhodium, palladium, and molybdenum are not removed in the melt-refining process. Control of their concentrations is effected by their removal from a sidestream of material made up largely of the crucible residue (skull). Iron, nickel, and chromium which may be introduced by inclusion of small amounts of the stainless-steel cladding material were found to behave in a manner similar to that of the noble fission products.[25]

After melt refining is completed, the purified metal is poured into a graphite mold. The use of mold coatings is not planned because of the difficulty of remote application of such coatings. However, if experience shows it to be desirable, one of the mold coatings that can be used is magnesium zirconate. Flame-sprayed magnesium zirconate coatings have been tested on heated graphite molds in uranium production operations and found to increase mold life and ingot quality.[28,30]

Fundamental Studies of Liquid-Metal and Salt Systems

Increasing attention is being given to the use of liquid-metal and salt systems as media for the processing of nuclear fuel materials. In two-phase metal and salt systems, selective oxidation and reduction reactions may be utilized to effect desired separations. In addition to selective extraction by salt or metal phases, purification and recovery of nuclear fuel materials may also be effected by selective crystallization, volatilization, selective compound formation, and extraction between immiscible metal phases. The metal solvents employed generally have sufficiently high volatility to permit their ready removal from the product material by evaporation. The metals most generally employed as solvents for uranium-, plutonium-, or thorium-based fuel materials are zinc, cadmium, mercury, and magnesium.

Solubilities in Liquid-Metal Systems. Knowledge and understanding of the basic chemical and metallurgical phenomena in liquid-metal and fused-salt systems are requisite to the design of processes. The solubilities of fission-product, fissionable, and structural elements are of prime importance. Two thermodynamic analyses of solubility in liquid-metal systems have been reported.[31,32]

The solubilities of selected fissionable and fission-product elements were measured in mercury (Table III-4)[33] to devise a plutonium–fission-product separation process in mercury solvent (see process description and performance below). The uranium solubility in bismuth ranged[34] from 0.09 to nearly 2 wt.% over the temperature range 350 to 600°C. Effects on the uranium solubility in bismuth of zirconium, magnesium, sodium, and fission-product elements were also determined. A progress report is also available on an investigation of thermodynamic and solubility relations in bismuth systems.[35] The preliminary solubility measurements in zinc, which subsequently led to the development of processes using zinc-based alloys at ANL, have been published.[36] Recent additions[25] to the fund of solubility information are the following:

Table III-4 SOLUBILITIES OF SELECTED ELEMENTS IN MERCURY[33]

Element	Temp., °C	Solubility, g of solute per liter of Hg
Zr	350	<0.001
Nb	350	<0.001
Mo	350	<0.001
Fe	350	0.002
Ta	350	<0.001
Pu	20	2.65
	150	20.0
	325	85.7
Ru	20	<0.002
	250	<0.002
La	20	2.87
	150	22.9
	250	37.0
Ce	20	1.31
	150	19.8
	250	74.5

1. The solubility of iron in cadmium ranged from 6×10^{-5} at.% at 322.6°C to 4.5×10^{-3} at.% at 647.0°C. No evidence was found for the existence of any iron-cadmium intermetallic compounds.

2. The solubility of titanium in cadmium varied from 2.6×10^{-4} at.% at 420°C to 3.5×10^{-3} at.% at 735°C. In the titanium-cadmium system, two intermediate phases (Ti_2Cd and TiCd) have been identified.

3. Preliminary values for the solubility of vanadium in zinc increased from 0.14 per cent at 448°C to 0.71 per cent at 656°C. The stoichiometric formula VZn_3 has been assigned to the intermetallic compound.

Nature and Properties of Metals and Intermetallic Compounds. Zinc-based systems are frequently employed in liquid-metal processes. Therefore, over the past several years, determination of the nature and the properties of the uranium-zinc intermetallic compounds has occupied considerable attention. The structure of U_2Zn_{17} (delta phase) has been reported.[37] A second intermetallic compound richer in zinc has been identified. This compound, which has the approximate composition, U_2Zn_{23}, and which has been designated as the epsilon phase, has been identified[23,25] (see Fig. III-5), and work is under way to determine its position in the phase diagram and other pertinent properties.

Thermodynamic information of interest has been reported on (1) the mercury–mercuric chloride system,[38] (2) thermodynamic properties of liquid-metal solutions of antimony-cadmium-tin,[39] and (3) thermodynamic functions for the UCd_{11} intermetallic compound formed in a

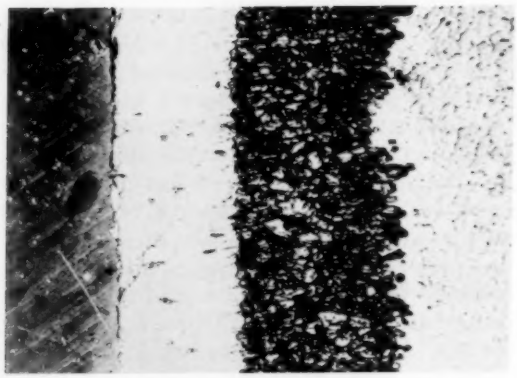

Fig. III-5 The reaction layer formed[25] between a uranium rod and molten zinc after 20 hr at 618°C.

uranium-cadmium system[25] and for yttrium-zinc compounds.[40]

The following material on liquid-metal physical properties is available: (1) the viscosity of zinc over the temperature range 421 to 823°C (Table III-5),[41] (2) a review article on diffusion in metals,[42] and (3) a series of Russian articles in which the structure of liquid metals is discussed.[43] A bibliography of 179 reports on liquid metals, including reports up to September 1960, is available from the Office of Technical Services.[44] Research has been initiated at Mound Laboratory to determine the density, viscosity, thermal capacity, and phase equilibria of plutonium and plutonium alloys that may be considered for use in power reactors. The viscosity of molten plutonium (99.95 per cent pure) has been determined in the temperature interval 648 to 950°C (see Table III-6).[45]

Distribution of Elements Between Immiscible Phases. Measurements are being made of the distribution of various elements between immiscible pairs of liquid metals, with the view to possible application of liquid-metal solvent extraction in pyrometallurgical processing. The ratio of the uranium distribution coefficient to that of several fission products in the zinc-bismuth or zinc-lead system has not been large enough for effective separation; therefore the influence of additive elements to one of the phases is being investigated.[25] Bismuth additions to a lead-zinc system increased the mutual solubility of the phases somewhat but markedly reduced the uranium distribution into the zinc phase (see Fig. III-6).

Table III-5 VISCOSITY OF LIQUID ZINC[41]

Run No.	Temp., °C	Density, g/cm^3	Viscosity, centipoises
1	823	6.206	1.72
2	759	6.260	1.77
1	716	6.306	1.96
2	660	6.356	2.07
1	601	6.414	2.28
2	553	6.456	2.54
1	496	6.516	3.07
2	480	6.531	3.12
1	446	6.562	3.66
1	432	6.574	3.68
2	430	6.580	3.37
1	428	6.578	3.72
1	421	6.582	3.71

Table III-6 VISCOSITY OF MOLTEN PLUTONIUM[45]

Run No.*	Temp., °C	Viscosity, centipoises
2	950	3.97
1	917	4.03
2	902	4.11
2	859	4.27
1	824	4.43
2	809	4.51
2	765	4.66
1	739	4.90
2	712	5.10
1	699	5.55
2	670	5.46
1	650	6.00
2	648	6.02
1	648	5.92

*Run 1, July 1960; run 2, January 1961.

Data have been reported[46] on the distribution of protactinium between a magnesium–38 per cent thorium liquid and uranium or a uranium–5.2 per cent chromium liquid (Table III-7). The data showed that over 99 per cent of the protactinium present will follow the uranium-rich phase in the separation of uranium from irradiated thorium by extraction with magnesium.

Moore at Hanford has investigated the distribution of uranium in the system aluminum–aluminum chloride–alkali chloride.[47] The distribution of uranium was found to be strongly dependent on flux composition, exhibiting a maximum in favor of the metal phase at aluminum chloride to alkali chloride mole ratios

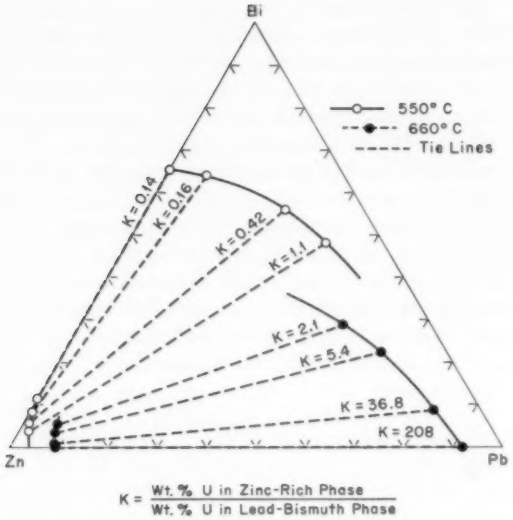

Fig. III-6 Distribution of uranium between a zinc-rich phase and a lead-bismuth phase.[25]

Table III-7 DISTRIBUTION OF Pa^{233} BETWEEN MAGNESIUM–38 WT.% THORIUM AND URANIUM OR URANIUM–5.2 WT.% CHROMIUM PHASES[46]

Charge		Distribution coefficient*	Pa extracted from Mg phase, %
Grams	Phase		
26.5 94.4	Mg–38% Th U	91	99.7
33.1 90.8	Mg–38% Th U	74, 46	99.5, 99.6
62.0 101.5	Mg–38% Th U–5.2% Cr	72	99.2
66.6 96.5	Mg–38% Th U–5.2% Cr	159	99.6
33.2 86.7	Mg–38% Th U–5.2% Cr	193	99.8

*Distribution coefficient = concentration of protactinium in uranium phase divided by that in magnesium phase (weight basis).

of 1 (see Fig. III-7). The alkali chlorides were found to be not simply inert diluents but a strong influence on the uranium distribution. Uranium distribution in favor of the metal phase increased as the size of the alkali cation increased, a fact attributed to differences in the polarizing capacity of the cation. In the system cesium chloride–aluminum chloride–aluminum, reduction of uranium chloride to metal can be greater than 99 per cent complete at equal phase weight ratios.

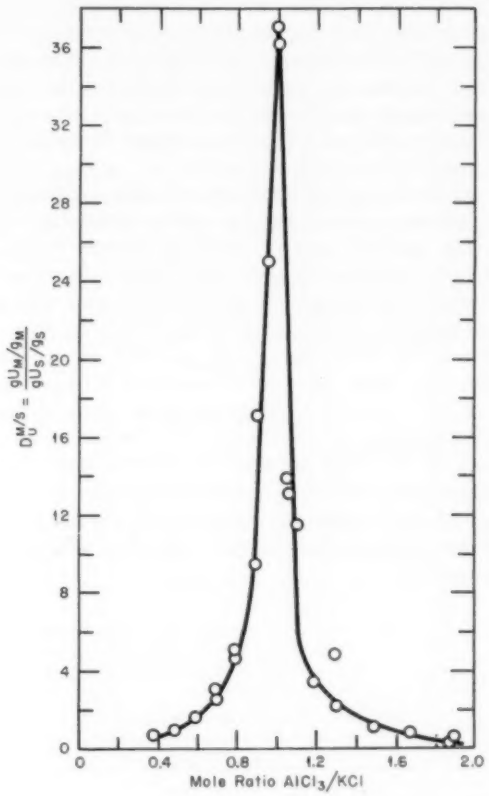

Fig. III-7 Distribution[47] of uranium in the system potassium chloride–aluminum chloride–aluminum at 725°C.

Equilibrium Constants for Oxidation and Reduction Reactions. Oxidation-reduction reactions between fused salts and liquid metals are being investigated in many pyrometallurgical processes to effect desired separations. The considerable work by Chiotti at Ames Laboratory directed toward the separation of various impurities from uranium by oxidation-reduction reactions between zinc and a fused potassium chloride–lithium chloride eutectic salt is summarized[48] in Tables III-8 and III-9. Equilibrium constants for the reactions attempted were calculated on the basis that Henry's law is applicable and that the mole fractions of the reactants and products are equal to or less than 0.015. Measured equilibrium constants (K) differ from those calculated directly from the free-energy data (K_N) by factors as high as 10^{15} (Table III-9). Examination of the activity coefficients makes these large differences plausible.

The activity coefficient for chromium in zinc was estimated from the phase diagram given in Hansen,[49] whereas activity coefficient ratios for other solutes in liquid zinc are based on the free-energy data for the intermetallic zinc compounds and the solubilities of these compounds in zinc.

On the assumption that the activity coefficient for uranium trichloride in a dilute concentration in the eutectic salt is unity at 500 and 700°C, activity coefficients were calculated for the other chlorides involved in these reactions. The values calculated for zinc chloride and chromium chloride differ by factors of 10 to 100 from values obtained from electromotive-force data. This was not considered surprising in view of the uncertainties in: (1) the data for the free energies of the chlorides and the intermetallic zinc compounds, (2) the solubilities, and (3) the equilibrium constants, all of which are involved in the calculation of the activity-coefficient ratios.

The possibility of achieving effective separations by multiple oxidation-reduction equilibrations between a zinc system and a potassium chloride–lithium chloride system is being analyzed on the basis of the data in Table III-9. The separation of thorium from uranium in a thorium–1 wt.% uranium alloy appears promising.[39]

Equilibrium constants have also been determined over the temperature range of 300 to 500°C for the reduction of uranium dioxide by magnesium dissolved in bismuth.[50] The kinetics of oxidation of uranium and magnesium in bismuth solutions were also investigated.

Reduction of Oxides by Liquid Metals. Reduction reactions, particularly those by which oxides may be reduced directly, are the key to the successful recovery and purification of fissionable material in several pyrometallurgical processes. For example, the selective reduction of compounds of the noble fission-

Table III-8 EQUILIBRIUM CONSTANTS, K_N, FOR OXIDATION-REDUCTION REACTIONS IN A KCl-LiCl/ZINC SYSTEM[48]

Reaction	Components in system	Temp., °C	$K_N (N \leq 0.015)$
$U + ThCl_3 \rightarrow UCl_3 + Th$	U, Th, Zr	700	9.0 ± 1.3
	Th, U	700	8.8 ± 0.6
	U, Th, Pa*	500	2.0 ± 0.5
	U, Th, Zr	500	2.3 ± 1.3
$Ce + UCl_3 \rightarrow CeCl_3 + U$	Ce, U, Zr	700	10.8 ± 2.0
	Ce*, U	500	9.1
	Ce, U	500	18
$Zr + \frac{3}{2}ZnCl_2 \rightarrow ZrCl_3 + \frac{3}{2}Zn$	U, Th, Zr	700	2.0×10^3
	U, Th, Zr	700	3.2×10^3
	Zr, Cr	700	1.5×10^3
	Ce, U, Zr	700	1.7×10^3
	Zr, U	650	1.8×10^3
	Zr, Cr	500	1.5×10^3
	U, Th, Zr	500	4.0×10^3
	Zr	500	1.9×10^3
$Zr + \frac{3}{2}CrCl_2 \rightarrow ZrCl_3 + \frac{3}{2}Cr$	Zr, Cr	700	68 ± 15
	Zr, Cr	500	280 ± 40
$Cr + ZnCl_2 \rightarrow CrCl_2 + Zn$	Zr, Cr	700	7.6 ± 2.0
	Cr, U	650	4.5
	Cr, U	625	5.1
	Zr, Cr	500	3.0 ± 1.5
$Th + PaCl_3 \rightarrow ThCl_3 + Pa$	Th, U, Pa*	500	10.0 ± 6.0
$U + PaCl_3 \rightarrow UCl_3 + Pa$	Th, U, Pa*	500	20.0 ± 1.3
$Y + UCl_3 \rightarrow YCl_3 + U$	U, Y*	500	1.0 ± 0.5
$Th + ZrCl_3 \rightarrow ThCl_3 + Zr$	Th, U, Zr	500	$\sim 3.5 \times 10^3$
		700	75 ± 25
$Th + \frac{3}{2}ZnCl_2 \rightarrow ThCl_3 + \frac{3}{2}Zn$	Th	700	$6.0 \times 10^{5\pm1}$

*Radioactive tracer added; concentrations in the zinc and salt phases determined radiochemically.

product elements, as in the noble-metal extraction step of the EBR-II skull reclamation process (see Fig. III-8), provides separation of these elements from uranium. Much more difficult is the direct reduction of the relatively stable oxides of the fissionable materials, uranium, plutonium, and thorium. However, at ANL complete reductions of uranium oxides with magnesium-zinc alloys have been consistently realized in the presence of a suitable flux.[23] The composition of flux plays an important role in promoting rapid and complete reductions. Some of the variables affecting the rate and extent of reduction of uranium fissium oxides by zinc-magnesium alloys in the presence of a flux have been investigated.[25] Complete reduction of thorium oxide has also been achieved with a 5 per cent magnesium-zinc alloy in the presence of a suitable flux.[25] Preliminary observations have indicated that separation of plutonium and rare-earth elements may be possible through selective reduction of the oxides from a halide flux using high magnesium–zinc systems.[25]

Hewitt, in a study of the reduction of uranium oxides with magnesium-zinc alloys in the absence of a flux, realized incomplete and slow reductions.[51] Maximum reductions were found at magnesium concentrations of 6 to 14 per cent. It was concluded that the reaction was too slow and incomplete to be of practical value in the production of uranium. The partial reduction of thoria by magnesium dissolved in lead and bismuth was observed by Broomfield and others in convection loops.[52] The resulting intermetallic compounds plugged the loop.

Development of Liquid-Metal and Salt Processes

The solubilities of selected fissionable and fission-product elements in mercury measured at Los Alamos[33] (see Table III-4) indicated that purification of plutonium fuels in mercury

Table III-9 CALCULATED VALUES FOR THE ACTIVITY-COEFFICIENT RATIOS FOR CHLORIDE SOLUTES IN DILUTE KCl-LiCl EUTECTIC SOLUTIONS[48]

Reaction	Temp., °C	$\Delta F°$, kcal	K	K_N	Activity-coefficient ratios: Metals	Activity-coefficient ratios: Chlorides
					Th/U	$UCl_3/ThCl_3$
$U + ThCl_3 \rightarrow UCl_3 + Th$	500	+15.6	3.87×10^{-5}	2.0	1.66×10^{-5}	1.16
	700	+15.3	3.65×10^{-4}	9.0	1.02×10^{-4}	0.40
					1/Cr	$CrCl_2/ZnCl_2$
$Cr + ZnCl_2 \rightarrow CrCl_2 + Zn$	500	+3.0	1.40×10^{-1}	3.3	1.5×10^{-2}	2.87
	700	+4.1	1.20×10^{-1}	7.5	3.7×10^{-2}	0.43
					1/Zr	$ZrCl_3/(ZnCl_2)^{3/2}$
$Zr + \frac{3}{2}ZnCl_2 \rightarrow ZrCl_3 + \frac{3}{2}Zn$	500	−56.5	1.01×10^{16}	1.90×10^{3}	7.1×10^{6}	7.40×10^{5}
	700	−54.3	1.59×10^{12}	1.5×10^{3}	2.72×10^{3}	3.90×10^{5}
					$(Cr)^{3/2}/Zr$	$ZrCl_3/(CrCl_2)^{3/2}$
$Zr + \frac{3}{2}CrCl_2 \rightarrow ZrCl_3 + \frac{3}{2}Cr$	500	−61.1	1.78×10^{17}	3.17×10^{2}	3.88×10^{9}	1.50×10^{5}
	700	−60.5	3.93×10^{13}	7.30×10	3.81×10^{5}	1.41×10^{6}
					Zr/U	$UCl_3/ZrCl_3$
$U + ZrCl_3 \rightarrow UCl_3 + Zr$	500	−5.1	2.77×10	6.92×10^{3}	5.48×10^{-4}	7.30
	700	−4.4	9.73	6.75×10^{2}	2.80×10^{-2}	0.52
					Zr/Th	$ThCl_3/ZrCl_3$
$Th + ZrCl_3 \rightarrow ThCl_3 + Zr$	500	−20.7	7.14×10^{5}	3.46×10^{3}	3.31×10	6.23
	700	−19.7	2.67×10^{4}	0.75×10^{2}	2.75×10^{2}	1.30
					$(Cr)^{3/2}/U$	$UCl_3/(CrCl_2)^{3/2}$
$U + \frac{3}{2}CrCl_2 \rightarrow UCl_3 + \frac{3}{2}Cr$	500	−66.2	5.26×10^{18}	2.17×10^{6}	2.13×10^{6}	1.14×10^{6}
	700	−64.9	3.83×10^{14}	4.93×10^{4}	1.07×10^{4}	7.26×10^{5}
					1/Th	$ThCl_3/(ZnCl_2)^{3/2}$
$Th + \frac{3}{2}ZnCl_2 \rightarrow ThCl_3 + \frac{3}{2}Zn$	500	−77.2	6.79×10^{21}	6.60×10^{6}	2.35×10^{8}	4.38×10^{6}
	700	−74.0	4.24×10^{16}	1.13×10^{5}	7.46×10^{5}	5.03×10^{5}
					U/Y	UCl_3/YCl_3
$Y + UCl_3 \rightarrow YCl_3 + U$	500	−22.9	2.99×10^{6}	1.0	4.65×10^{7}	6.43×10^{-2}

would be possible provided that no difficulties were encountered with dissolution or coprecipitation. Therefore a process was devised (Fig. III-9) and carried out on a 10-g-plutonium scale with samples of plutonium-iron-fissium alloy which contained typical fission-product elements in amounts corresponding to 10 per cent burnup of the plutonium. The results in Table III-10 indicate good purification of all elements except lanthanum and cerium which coprecipitated with the plutonium in the recrystallization step. For this reason a simple dissolution-extraction process was concluded to be inadequate for this fuel.

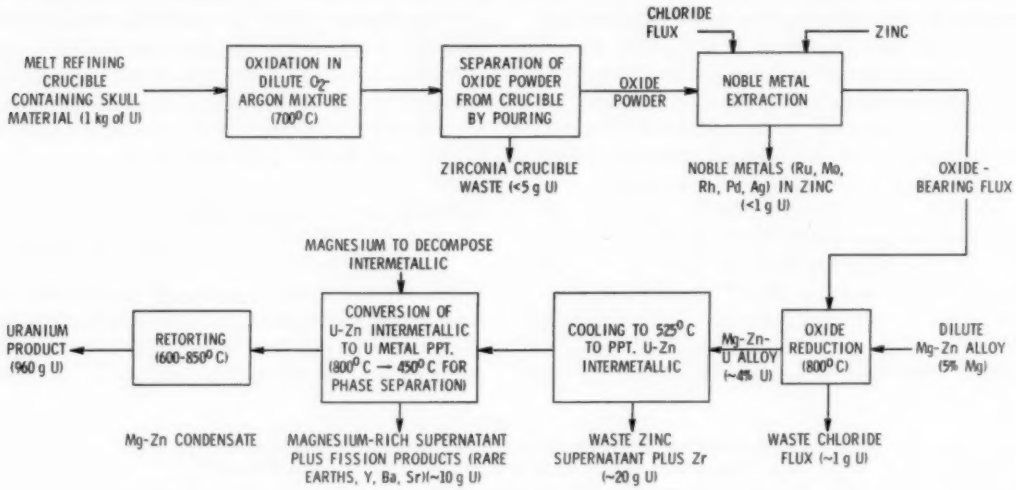
CHLORIDE FLUX
ZINC
MELT REFINING CRUCIBLE CONTAINING SKULL MATERIAL (1 kg of U)
OXIDATION IN DILUTE O_2-ARGON MIXTURE (700°C)
SEPARATION OF OXIDE POWDER FROM CRUCIBLE BY POURING
OXIDE POWDER
NOBLE METAL EXTRACTION
ZIRCONIA CRUCIBLE WASTE (<5 g U)
NOBLE METALS (Ru, Mo, Rh, Pd, Ag) IN ZINC (<1 g U)
OXIDE-BEARING FLUX
MAGNESIUM TO DECOMPOSE INTERMETALLIC
URANIUM PRODUCT (960 g U)
RETORTING (600-850°C)
CONVERSION OF U-Zn INTERMETALLIC TO U METAL PPT. (800°C — 450°C FOR PHASE SEPARATION)
COOLING TO 525°C TO PPT. U-Zn INTERMETALLIC
Mg-Zn-U ALLOY (~4% U)
OXIDE REDUCTION (800°C)
DILUTE Mg-Zn ALLOY (5% Mg)
Mg-Zn CONDENSATE
MAGNESIUM-RICH SUPERNATANT PLUS FISSION PRODUCTS (RARE EARTHS, Y, Ba, Sr)(~10 g U)
WASTE ZINC SUPERNATANT PLUS Zr (~20 g U)
WASTE CHLORIDE FLUX (~1 g U)

Fig. III-8 EBR-II liquid-metal process for reclamation of melt-refining skulls.

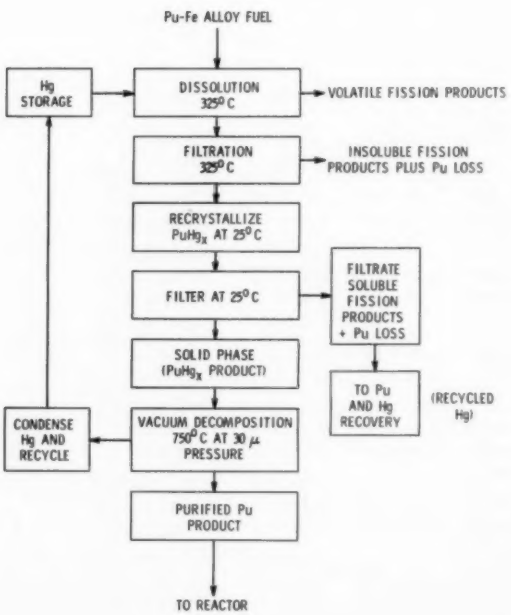

Fig. III-9 Flow sheet for processing of plutonium-iron alloy fuel by recrystallization.[33]

Table III-10 PURIFICATION OF PLUTONIUM-IRON-FISSIUM ALLOY BY RECRYSTALLIZATION FROM MERCURY[33]

Element	Concentration of element, wt.%	
	Fissium alloy	Final product
Pu	91.3	98.3
Fe	2.37	0.060
Zr	0.67	0.019
Nb	0.04	Not detected
Mo	0.75	0.0088
Ru	0.97	Not detected
La	1.59	1.06
Ce	0.74	0.53

To overcome the disadvantage of poor rare-earth separation, a halide-flux extraction step was incorporated into the flow sheet following the dissolution step. The salt flux employed was composed of 70 wt.% rubidium chloride and 30 wt.% lithium chloride. This system melts at 310°C. The rare earths were oxidized with ferrous chloride and extracted into the salt phase. A 10 per cent excess of ferrous chloride was employed and was equivalent to less than

0.7 per cent of the plutonium. The salt-metal phase separation was effected at 300°C in order that the salt phase would be frozen. The results given in Table III-11 indicate that adequate removal of fission products including rare earths can be effected by this combined slagging-crystallization procedure.

Table III-11 PURIFICATION OF PLUTONIUM-IRON-FISSIUM ALLOY BY COMBINED SLAGGING-RECRYSTALLIZATION PROCESS[33]

(38 g Salt Phase, 9.3 g Fissium Alloy, 100 ml Hg)

Element	Concentration of element, wt.%		
	Fissium alloy	Plutonium product	Decontamination factor
Pu	91.3	99.7	
Fe	2.54	Not detected	>2540
Zr	0.77	Not detected	>770
Mo	0.89	0.008	120
Ru	1.30	Not detected	>1300
La	2.13	0.11	21
Ce	1.02	0.08	14

A plutonium-cerium-cobalt ternary system has also been proposed as a fuel for power reactors. The cobalt concentration is approximately 12 to 25 at.%, whereas the concentration of plutonium can be varied over a wide range without seriously affecting the melting point of the system. Since cerium is present in gross amounts as an alloying constituent, it seems likely that the removal of soluble rare-earth fission products would not be necessary for such fuels, under which condition the flow sheet shown in Fig. III-9 would be applicable. In a run in which this procedure was used, the product contained 90 to 95 per cent of the plutonium initially present. Its chemical composition was 97 per cent plutonium, about 3 per cent cerium, and 0.2 per cent cobalt.

In the above experiments, yields of 80 to 96 per cent of the total plutonium were obtained, which are good considering the small scale of the experiments. Plutonium was obtained as a metallic button by heating the final plutonium-mercury concentrate to 750°C for 2 hr in a vacuum.

Pyrex was used as a container material for most of the experiments in the temperature range of 25 to 325°C. For the vacuum decomposition step, the mercurides were contained in either tantalum or magnesia crucibles within a stainless-steel tube. The plutonium-cerium-cobalt alloy dissolution and filtration experiments were conducted in type 304 stainless-steel equipment. In mercury solutions typical of those which result after dissolution of the fuel, corrosion rates at 340°C (boiling solutions) were less than 0.10 in. per year for the stainless steel and less than 0.005 in. per year for tantalum.

It is planned to use an auxiliary process with the melt-refining process in the EBR-II fuel cycle to recover and purify residual fuel material remaining in the melt-refining crucible. This material, known as skull material, is freed from the crucible by controlled oxidation at 800°C to convert it to a free-flowing powder. In experiments at Argonne, incorporation of a noble-metal extraction step in the skull reclamation process (see Fig. III-8) resulted in considerable improvement in the separation of noble-metal fission products (ruthenium, rhodium, palladium, and molybdenum) from uranium.[25] In this step the relatively noble fission products are extracted into zinc from a slurry of skull oxides in a molten halide flux. Uranium losses in this step are negligible. (A patent has been granted on a similar procedure in which no flux was employed.[51]) Over-all process fission-product removals ranged from 77 per cent for ruthenium to 99 per cent for palladium (Table III-12). These were considered to be adequate for purposes of the EBR-II fuel cycle.

Table III-12 FISSION-PRODUCT REMOVALS EFFECTED BY EBR-II SKULL RECLAMATION PROCESS[25]

Constituent	Conc. in starting material,* wt.%	Conc. in product, wt.%	Removal, %
Ce	3.2	0.25	92
Zr	1.2	0.2	84
Mo	2.2	0.3	87
Ru	1.7	0.4	77
Pd	0.18	$<10^{-3}$	99

*Oxygen-free basis.

In expectation that future core loadings of the EBR-II reactor will employ plutonium as the fissionable material, work is under way at ANL to achieve satisfactory separation of rare-earth elements from plutonium. One method that

shows promise is selective reduction of the oxides from a halide flux using high magnesium–zinc systems.[25] Another method is based on the insolubility of plutonium in molten calcium and the anticipated adequate solubilities of rare-earth elements. Cerium solubilities in zinc solutions containing 26 to 77 wt.% calcium are adequate for decontamination of plutonium from cerium and probably other rare-earth elements provided that plutonium can be completely precipitated and undesirable coprecipitation effects do not interfere.

A process is now under development at ANL for the isolation of plutonium bred in the uranium blanket material of the EBR-II reactor. The basis on which a plutonium-uranium separation is sought is the solubility of plutonium in magnesium-rich zinc alloys and the contrasting low solubility of uranium in these alloys. Work has been reported[25] on a procedure that utilizes, for the initial dissolution step, the high solubility of uranium in 12 to 15 per cent magnesium–zinc alloys (see Fig. III-10). In such alloys,

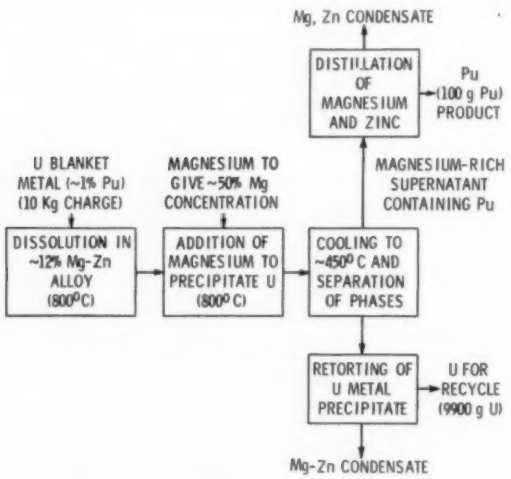
Mg, Zn CONDENSATE
DISTILLATION OF MAGNESIUM AND ZINC
Pu (100 g Pu) PRODUCT
U BLANKET METAL (~1% Pu) (10 Kg CHARGE)
MAGNESIUM TO GIVE ~50% Mg CONCENTRATION
MAGNESIUM-RICH SUPERNATANT CONTAINING Pu
DISSOLUTION IN ~12% Mg-Zn ALLOY (800°C)
ADDITION OF MAGNESIUM TO PRECIPITATE U (800° C)
COOLING TO ~450° C AND SEPARATION OF PHASES
RETORTING OF U METAL PRECIPITATE
U FOR RECYCLE (9900 g U)
Mg-Zn CONDENSATE

Fig. III-10 EBR-II liquid-metal process for uranium blanket metal.[25]

uranium may be rapidly and completely dissolved to give final uranium concentrations of 14 per cent or more. The uranium may subsequently be precipitated while the plutonium remains in solution by addition of magnesium to a 50 per cent concentration. Recovery of the valuable constituents is effected by separation of the phases and vaporization of the solvent metals. In a demonstration of this process with a 1 per cent plutonium–uranium alloy[25] (400 g), the alloy was easily dissolved. When magnesium was added to a 50 per cent concentration and the solution cooled to 400°C, 99.7 per cent of the uranium was precipitated while all of the plutonium, within analytical error, remained in solution. The phases were separated, and the uranium precipitate was washed once with fresh 50 per cent magnesium–zinc alloy. High recovery and good separation of plutonium was shown to be possible by this procedure.

At Atomics International new methods are being sought for processing thorium fuels. In an investigation of solid-state thermal diffusion,[53] a rod of thorium–1 per cent uranium alloy was heated in a temperature gradient (1100 to 1400°C), under which condition the uranium was expected to diffuse to the hotter end of the rod. Contrary to expectations the uranium concentration increased slightly in the cooler end of the rod. Essentially no uranium concentration change occurred in five solid-state zone refining runs in which a hot zone at a temperature of 1350°C was passed at a rate of 1 in./hr along a 6-in.-long by $\frac{3}{4}$-in.-diameter rod.[54]

In an electrorefining process being investigated at Atomics International, impure thorium is dissolved anodically into a fused-salt bath and deposited along with any uranium present in a molten zinc cathode. Seven electrorefining runs were carried out with lightly irradiated material, each run corresponding to about a one-half throughput of the thorium[54] (as $ThCl_4$). Qualitatively, some decontamination of the thorium was achieved since the radiation levels of the zinc cathode were considerably lower than those of the initial anode rods.

The separation of uranium from metallic thorium blanket material by a molten magnesium extraction process is also being studied at Atomics International. Thorium may be dissolved in magnesium, whereas the uranium is very insoluble. Any protactinium present will accompany the uranium[46] (see Table III-7). The magnesium extract that contains the thorium is reacted with hydrogen to form thorium hydride, which is then separated by filtration. The supernatant liquid, which contains about 8 wt.% thorium, is then recycled to the dissolution step. At the present time, attempts to separate the uranium precipitate by filtration are being made.[54] Filtration through 20- and 35-μ filters

resulted in recovery of about 95 per cent of the uranium, but the thorium-to-uranium ratio in the precipitate ranged from 10 to 18, which is much higher than anticipated. Filtration through a 65-μ filter decreased uranium recovery to less than 50 per cent. Washing of the uranium precipitate will be attempted to reduce the thorium-to-uranium ratio.

Construction Materials

Pyrometallurgical processes require the containment of liquid metal and fused salts generally at elevated temperatures. Often the corrosion conditions are severe. Therefore the evaluation and testing of construction materials is an important adjunct to process development.

The processing system developed by Brookhaven National Laboratory for the Liquid Metal Fuel Reactor (LMFR) fuel (liquid bismuth containing 1000 ppm uranium, 350 ppm magnesium, and 250 to 300 ppm zirconium) is based on contacting the fuel with a molten chloride salt system containing bismuth trichloride as an oxidant. Extensive corrosion tests have been made in static and tilting furnaces and in thermal- and forced-convection loops.[55] The effect of exposure to the two-phase metal–fused salt environment has been explored both with and without the presence of bismuth trichloride in the salt phase. Typical corrosion results are shown in Table III-13. In the absence of bismuth trichloride, a number of materials have suitable corrosion resistance. These include mild steel, 400-series stainless steels, and the chromium-molybdenum alloys. Rates of attack, in general, are no different for simultaneous exposure to eutectic salt and bismuth fuel than for exposure to eutectic salt alone.

The addition of even small quantities of bismuth trichloride increases melt corrosiveness to the point where none of the above materials is satisfactory. Only gold showed reasonable resistance, and this would require further testing for possible plant application. In tests made with molybdenum and tantalum, residual bismuth trichloride contents were too low for the results to have any significance.

In connection with the development of the skull reclamation process at ANL, tests have shown little or no corrosion of type 405 stainless steel by zinc-magnesium-cadmium systems at 750°C for zinc concentrations below 15 at.%, regardless of cadmium-magnesium ratios.[25] Above a zinc concentration of 15 at.%, the rate of corrosion increases sharply as the zinc concentration increases. In this same system at 850°C, tantalum showed good corrosion resistance at zinc

Table III-13 TYPICAL CORROSION IN PROCESSING LMFR FUEL WITH FUSED CHLORIDE SALTS[55]

[Molten Salt: NaCl-KCl-$MgCl_2$ Eutectic (Plus 5% $BiCl_3$ Where Indicated); Test Lengths: 600 to 6000 Hr]

Metal	Temp., °C	Type of test	Type of attack	Max. rate of corrosion, mils/yr
		No $BiCl_3$		
S.S. 347	500–575	Thermal convection	Intergranular	0.5–4
S.S. 347	520	Forced convection	Transgranular	1.3
S.S. 410	495–570	Thermal convection	Transgranular	2–3
$2^1/_4$ Cr–1 Mo	500	Thermal convection	Transgranular and intergranular	3
SAE 1020	500	Tilting furnace		None observed
		With 5% $BiCl_3$*		
Molybdenum	500	Tilting furnace	Pitting	2
Molybdenum	500	Tilting furnace	Transgranular	2
Tantalum	500	Tilting furnace	Pitting	1.4
Tantalum	500	Tilting furnace	Transgranular	1.8
Gold	500	Tilting furnace	Intergranular	1.0

*Residual $BiCl_3$ content was <0.3 per cent in all tests except gold; residue from gold test exceeded 4.9 per cent.

concentrations up to about 75 per cent, at which concentration slight attack was noted. At a 98 wt.% zinc concentration, the attack on tantalum was severe. In a 95 per cent zinc system, sintered molybdenum was severely attacked while tungsten was unattacked.

Solution stability runs have shown that graphite (grades CS and ATJ) reacts too rapidly with uranium dissolved in magnesium-zinc solutions to be usable as a crucible material for containing the skull reclamation process solutions (see Fig. III-8). At 800°C considerable diffusion of zinc through graphite pores also occurs[25,26] and can lead to large zinc losses. Cladding the graphite with various materials, tantalum and tungsten being the most promising, was suggested by Hewitt[56] as a means of reducing or eliminating zinc loss by diffusion.

Corrosion-rate measurements of niobium by molten uranium-chromium eutectic are beginning at Ames.[40] In preliminary tests conducted in crucibles at 900, 950, and 1000°C, there is evidence that some niobium was dissolved by the uranium-chromium eutectic alloy.

Battelle Memorial Institute has been engaged in the development of container materials for plutonium alloys considered for use as fuel in the Los Alamos Molten Plutonium Reactor Experiment (LAMPRE). Various alloys have been evaluated metallurgically.[57] Preliminary corrosion data indicate that good resistance to attack by the molten plutonium fuels may be obtained by alloying tantalum with rhenium, tungsten, and yttrium. The yttrium alloys displayed good corrosion resistance even though most of the yttrium was lost during arc melting. Methods of alloy preparation and fabrication behavior of the various alloys are discussed in the report.

Embrittlement of metals under stress by liquid metals (stress corrosion) is a recognized cause of metal container failure. The rate of bismuth penetration into grain boundaries of polycrystalline nickel was significantly increased[58] when the nickel was under plastic strain. In an evaluation of this problem, Suss[59] doubts the practicality of establishing threshold values of stress as a means of eliminating

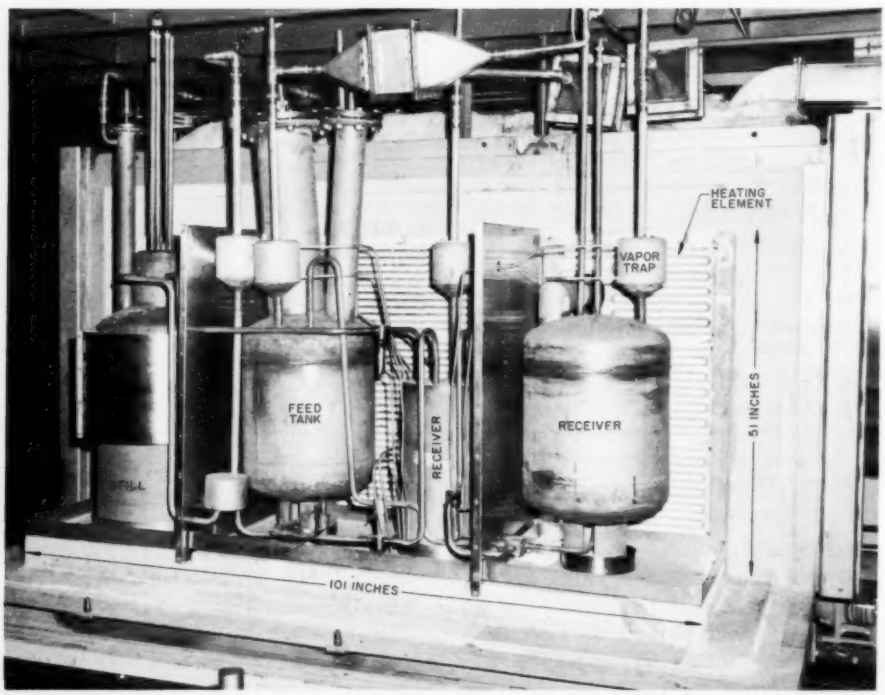

Fig. III-11 Large-scale cadmium distillation unit.[25]

stress corrosion and recommends selection of an alternate material less susceptible to stress corrosion.

Information on several nuclear engineering materials (uranium, plutonium, thorium, ceramic fuels, graphite, magnesium, beryllium and zirconium) has been assembled in the book, *Materials for Nuclear Engineers*.[60] A compilation of papers on physical and chemical properties, methods of fabrication, and irradiation behavior of carbon and graphite has also been issued.[61]

Equipment Development

A large-scale cadmium distillation unit, having a capacity of 100 kg/hr, was recently placed in operation at Argonne (see Fig. III-11).[25] This unit was constructed to provide engineering and operational experience in a unit operation important in many liquid-metal processes. In the first eight distillation runs, distillation rates were increased from 12 to 65 kg/hr. The metal vapors were condensed in an air-cooled condenser. In general, the unit has functioned well.

In fulfillment of an AEC contract, Aeroprojects, Inc., has reported on the possible application of ultrasonic activation in pyrometallurgical processing.[62] As compared to mechanical agitation, faster rates were found with ultrasonic agitation for dissolution of metals, equilibration of phases, reduction of uranium oxides contained in a halide salt by magnesium either alone or alloyed with another metal, wetting of solid phases, and dispersion of a solid phase within a liquid phase. The advantage of ultrasonic treatment is the ability to introduce vibratory energy without the use of mechanically moving parts. Designs were suggested for the transmittal of ultrasonic energy into radioactive environments.

A condenser design suitable for use in liquid-metal distillation units has been described by Burnet and Buchanan.[63] The temperature of the condensing surface was established by controlling the pressure over a boiling sodium-potassium eutectic alloy. The performance was evaluated in test units in which pure bismuth was distilled as the test material. In the actual test distillation apparatus, the condenser was used as an in-column condenser or cold finger. The vapors that condensed on the cold finger fell back into the pot as reflux. The amount of reflux was changed by adjusting the pressure over the boiling potassium–sodium alloy eutectic and therefore the temperature of the condensing surface. The remaining vapors were condensed in an external condenser.

A system for conveying liquid metals or radioactive liquids has been described in which vapors of the fluid being pumped are used to drive an injector type pump.[64]

An inductive or eddy-current method has been used to measure the sodium-potassium coolant level in a sealed system in the Dounreay fast reactor.[65]

Bottom-pour reusable crucibles made of tantalum or calcium fluoride-coated steel have been developed at Los Alamos for casting of plutonium and plutonium-rich alloys and have replaced ceramic crucibles for casting work on the kilogram scale.[66] A design for the cold-crucible induction melting of reactive metals has been demonstrated and reported by Schippereit and others.[67]

Other Nonaqueous Processes

Nearly all the nonaqueous fuel processes falling outside the volatility and pyrometallurgical categories are suitably described by the term "pyrochemical." Pyrochemical processes employ many of the same materials and techniques as pyrometallurgical schemes; they are distinguished by the difference that the fuel is not ordinarily in the metallic state through the various phases of the process. Pyrochemical methods, which have been applied primarily to oxide and carbide fuels, usually involve gases, molten salts, and liquid metals as process media. The potential economic advantages are common to both types of process, i.e., capability for handling short-cooled fuels, and a minimum of chemical conversion steps. Similarly, the principal disadvantage of both types of process is the necessity for remote fuel refabrication resulting from the relatively low, but adequate, fission-product removals.

Oxide Fuel Processing

The salt-cycle process, under development at Hanford as a part of the plutonium-recycle program, is based on an electrolytic procedure for processing uranium oxide–plutonium oxide fuel mixtures.[68–70] Four basic steps are included in the process flow sheet:

1. Dissolution of the oxide fuel in a molten chloride salt by sparging the system with chlorine or hydrogen chloride.

2. Selective electrodeposition of a fraction of the uranium as the dioxide, which is discarded as a by-product. This stream is essentially free of plutonium.

3. Codeposition of a mixture of uranium dioxide–plutonium dioxide with a higher plutonium-to-uranium ratio than in the initial feed.

4. Recycle of the enriched material to the reactor after the appropriate makeup and refabrication operations.

Treatment with chlorine diluted by nitrogen has been investigated as a possible method for the removal of Zircaloy cladding from the oxide fuel.[68,70] The strongly exothermic reaction can be controlled by regulating the flow rate and the amount of nitrogen diluent. In an experiment at 415°C, with an initial nitrogen-to-chlorine ratio of 4:1 decreasing to 1:2, the Zircaloy cladding was removed through the formation of volatile zirconium tetrachloride that collected as a condensate. This material contained only a small concentration of uranium (approximately 0.1 per cent).

The process flow sheet was demonstrated in an additional hot-cell experiment to examine the effects of (1) a higher temperature in the by-product deposition step (800°C, compared to 750°C in earlier runs) and (2) a dry air atmosphere on the product deposition step. In the by-product deposition, decontamination factors were ~140 for plutonium, ~600 for cerium, ~1600 for other rare earths, and ~1600 for strontium. Two uranium dioxide samples from the product deposition step showed plutonium-enrichment factors of 1.32 and 1.48 and decontamination factors of ~2 for cerium, 7 and 8 for other rare earths, and 130 and 250 for strontium. This plutonium enrichment is sufficient to establish a self-sustaining plutonium-recycle process. Although some rare-earth fission-product decontamination is achieved, repeated use of the salt would ultimately result in an accumulation of rare earths in a concentration that would prevent their removal from the product. A desirable solution to this problem would be to remove the rare earths with the uranium dioxide by-product; unfortunately no method of doing this appears to be available at present.

In the sodium chloride–potassium chloride system, a basis has been established for producing uranium dioxide deposits ranging from loosely packed aggregates of smooth-surfaced crystal grains to self-supporting, smooth-surfaced, polycrystalline compacts with densities as high as 98 per cent of the theoretical uranium dioxide crystal density.[68–70]

In the potassium chloride–lead chloride system, variations in the potassium-to-lead ratio from 1.0 to 2.5, and in temperature from 500 to 750°C, had little effect on the nature of the uranium dioxide product.[68] The deposits consisted of large, well-formed crystals with oxygen-to-uranium ratios less than 2.01 and lead contents of 200 to 1000 ppm. In the sodium chloride–magnesium chloride system, deposits were obtained having oxygen-to-uranium ratios less than 2.01 and magnesium contents[70] of about 50 ppm. The crystals were not as large or well formed as those obtained from the potassium chloride–lead chloride system, however. Decontamination factors for cerium in by-product depositions were 3.3 at 565°C and 10 at 614°C, in contrast to a value of ~200 at 750°C in the sodium chloride–potassium chloride system.

Several molten chloride salt systems are receiving consideration as possible process media. Although the principal emphasis has been on the sodium chloride–potassium chloride eutectic, other systems including potassium chloride–lead chloride, sodium chloride–magnesium chloride, and potassium chloride–magnesium chloride have also been considered with a view to obtaining a lower liquidus temperature.

The behavior of plutonium in the various salts has been investigated further. Attempts to achieve effective separation of rare earths from plutonium by electrodeposition of the metals were unsuccessful.[68] In potassium chloride–lead chloride, control of the plutonium behavior appears difficult in both the by-product and product deposition steps. In the former the plutonium decontamination factor was 12 to 25; in the latter the plutonium enrichment factor was about 0.5. Both these values are discouragingly low from a process viewpoint.

Several supplementary chemical studies have been undertaken to characterize the uranium species present in the chloride salt media. Spectrophotometric measurements on solid sodium chloride–potassium chloride containing

dissolved uranium were made at room temperature by means of a mulling technique.[70] Three closely spaced absorption peaks were found in the visible region at 423, 437, and 458 mμ. The relative intensities varied with different melt pretreatments, suggesting that three different species are involved. Further work in the infrared region has indicated a new peak at 11.6 μ, ascribed to U(VI), in addition to the normal peaks at 11.0 μ.

Studies in the sodium chloride–potassium chloride system show that the "cutoff" point beyond which alkali metals are deposited in preference to uranium is sensitive to the atmosphere.[69] It was possible to reduce the uranium concentration in the salt from 3.5 wt.% to about 0.5 wt.% under an air atmosphere and to 1.9 wt.% under a chlorine atmosphere before the cell resistance doubled. Side reactions are believed to occur as a result of melt-atmosphere interactions. Potential-current measurements on uranium-bearing sodium chloride–potassium chloride melts prepared by dissolving uranium dioxide (oxygen-to-uranium ratio = 2.1) with hydrogen chloride indicate three distinct reduction reactions. It is suspected that these are $UO_2^{2+}/UO_2(s)$, U(IV)/U(III), and U(III)/U(s). Chronopotentiometric determinations[69] suggest two probable mechanisms for the electrodeposition of uranium dioxide: (1) reversible electrolytic reduction and (2) electrically nonreversible chemical precipitation or electrophoresis. It is apparent that these systems are complex, with several different uranium species involved.

Differential thermal analysis was employed to establish the effect of dissolved uranyl chloride on the liquidus temperatures of the salt systems.[70] Marked lowering was found in potassium chloride–lead chloride at potassium-to-lead ratios of 2:1 to 3:1; a substantial increase was observed in sodium chloride–potassium chloride–magnesium chloride at sodium-to-potassium-to-magnesium ratios of 0.68:0.40:1; little effect was noted in potassium chloride–magnesium chloride at a potassium-to-magnesium ratio of 1.5:1.

Some engineering work has been reported on the salt-cycle process.[68–70] Gas lifts have performed satisfactorily in transferring sodium chloride–potassium chloride at 750°C between two 20-liter vessels. This technique is useful for mixing, salt transfers, and gas-salt contacting. In a scaled-up electrodeposition run utilizing 1 part lead chloride–2.5 parts potassium chloride, a 20-lb batch of uranium dioxide was prepared (oxygen-to-uranium ratio, 2.015; carbon, 300 ppm; potassium, 200 ppm; lead, 1000 ppm).

Construction of hot cave equipment to demonstrate the Atomics International low-decontamination process for high-burnup uranium dioxide fuels is nearing completion.[71,72] This project encompasses the entire fuel cycle, including decanning, processing, refabrication of fuel pellets, loading the pellets into capsules, and reirradiation. Studies of the effect of several irradiation-processing cycles on the composition of the fuel have been reported.[73]

In this fuel cycle, decanning is accomplished by oxidizing the uranium dioxide pellets, thereby converting the material to a fine powder. Either air or oxygen at reduced pressure produces the desired reaction at temperatures of 375 to 600°C. The effect of crystal dimensions on the mechanism and kinetics of the oxidation reaction has been discussed in a recent report.[74] The U_3O_8 powder is then reduced to uranium dioxide by hydrogen at 650°C. Several such oxidation-reduction cycles reduce the particle size of the oxide until it is suitable for the refabrication of new fuel pellets by cold pressing and sintering.[75] This technique has also been employed by Olin-Mathieson[76] to improve the sinterability of uranium dioxide. Although the principal objective of the process is to facilitate reenrichment and refabrication of the fuel, some fission-product removal is achieved, e.g., cesium, ruthenium, tellurium, iodine, and noble gases. Satisfactory reenrichment of reprocessed uranium dioxide by admixing enriched uranium dioxide powder has recently been demonstrated.[72]

The release of fission products during oxidation of uranium dioxide has been investigated at Oak Ridge[77] in connection with reactor safety studies. Uranium dioxide pellets were irradiated to tracer levels and then placed in a flowing air stream over a temperature range of 400 to 1500°C. At the lower temperatures the pellets were completely transformed to U_3O_8 powder. Above 1450°C, however, where uranium dioxide is the stable species, no mechanical degradation other than cracking was observed. Both iodine and the noble gases were retained to a greater extent under these circumstances. During oxidation, extensive release of ruthenium occurred, probably as the tetroxide. The chemistry of

ruthenium tetroxide has been clarified in some degree by recent measurements of its infrared spectrum,[78] from which thermodynamic functions for the ideal gas from 298.16 to 1000°K have been derived.

Sintered uranium dioxide pellets containing 10 wt.% thorium dioxide exhibit a marked resistance to oxidation, compared to pure uranium dioxide. Investigations were conducted at Atomics International[79] with a view to extending the low-decontamination oxidation-reduction process to thorium-containing fuels. Temperatures of 600 to 950°C and an oxygen pressure of 779 mm Hg were used. In the case of the thorium-containing fuel, the oxygen consumption was slow and linear over the entire temperature range, in contrast to the rapid and complex rate behavior observed with uranium dioxide alone. From 800 to 950°C the oxidation rate of uranium dioxide–10 wt.% thorium dioxide pellets is expressed as $R = 3.7 \times 10^{-3}$ exp $(-22{,}500/RT)$ moles $O_2/(cm^2)(min)$. No pulverization of the pellets occurred during the reaction.

Carbide Fuel Processing

The processing of uranium carbide fuels is under consideration at Atomics International.[53,71,72] The major research effort is being applied to a carbide-oxide-carbide cycle, in which the uranium carbide is oxidized at a moderate temperature (~400°C) and the resulting uranium dioxide is treated with carbon at a high temperature (above 1300°C) to regenerate uranium carbide as a sintered mass. This product is arc-melted to form a solid fuel material. The other process concept involves electrolysis of the uranium carbide in a lithium chloride–potassium chloride salt bath. The uranium is deposited as metallic dendrites on a molybdenum cathode. These are subsequently dissolved in mercury and converted to uranium carbide by reaction with propane.

In the carbide-oxide-carbide cycle, control of the reaction rate and dissipation of the heat in the oxidation phase have presented a more severe problem in kilogram-scale operations than was encountered in the oxidation of uranium dioxide fuels.[72] An additional complication is introduced by the necessity for removing and disposing of carbon dioxide formed in the reaction.

The oxidation reaction of arc-melted uranium carbide has been investigated by Murbach.[80] A rapid reaction, which is initiated at about 300°C in oxygen, produces an intermediate oxide with an oxygen-to-uranium ratio between 2.00 and 2.67. A second, slower reaction then takes place to produce U_3O_8. The oxidation is readily controlled by controlling the oxidizing atmosphere.

An oxidation-resistant form of uranium monocarbide has been encountered occasionally in material which has been freshly melted. Its oxidation rate is insignificant below 600°C, in contrast to the usual ignition temperature of about 250 to 400°C, depending mainly on particle size.[53,81] The oxidation-resistant form of the carbide is converted to the reactive form by exposure to moist air. Two experiments on the air oxidation of uranium monocarbide irradiated to 5000 and 15,000 Mwd/ton of uranium showed that the oxidation characteristics of irradiated material correspond to those of the reactive uranium carbide.

Both U_3O_8 and uranium dioxide have been converted to uranium monocarbide via carbothermic reduction.[53] In the case of U_3O_8, the carbon contents of the products were 5.09 and 5.67 wt.% in two experiments; for uranium dioxide the results were 4.50 and 4.53 wt.%. The theoretical carbon content of uranium monocarbide is 4.80 wt.%. It is suspected that the high values in the first two cases resulted from the use of graphite crucibles. The latter two results were obtained with molybdenum crucibles, which show little attack up to 1600°C. The reductions were all conducted at 1150°C for 2 hr in a hydrogen atmosphere.

The effect of the uranium dioxide preparation procedure on the carbothermic reduction is being investigated.[53] There is some evidence that the presence of fission-product oxides in the starting material affects the pyrophoricity of the carbide product.

Some other work on the reaction of uranium dioxide with graphite has been reported. Uranium dioxide pellets were exposed to graphite powder[82] at 1650 to 2130°C. From 1650 to 1760°C, a uranium monocarbide layer was formed on the pellets; at higher temperatures (1800 to 2000°C), uranium dicarbide was formed. In both cases the rate followed a parabolic law. In exploratory tests at Hanford[83] on the induction melting of uranium dioxide in graphite crucibles,

the product was contaminated with uranium monocarbide.

The preparation of stoichiometric uranium monocarbide by the addition of finely divided carbon to cadmium solutions of uranium at 550 and 700°C is being investigated.[84] The same result was obtained by adding carbon to a zinc solution containing uranium and 5 wt.% magnesium at 800°C.

A possible liquid-metal process for uranium carbide fuels has been suggested.[84] The carbide is burned in air or oxygen to produce oxide, which is processed by the scheme used for the decontamination and recovery of uranium in melt-refining skulls.[85] The carbide is regenerated by precipitation from a zinc or cadmium solution of uranium or by direct reaction of carbon with the normal metallic uranium product of the process.

Miscellaneous

Recent thermodynamic studies bearing rather directly on pyrochemical processes have been reported. The heat content, heat capacity, entropy, and Gibbs' free-energy function for thorium dioxide from 298.15 to 1200°K have been published.[86] Various thermodynamic properties, vapor pressures, and dissociation-pressure data have also been reported for niobium oxides,[87–89] cerium oxide,[90] zirconium dioxide,[91] and ruthenium tetroxide.[78] A bibliography on certain rare-earth oxides has been compiled.[91]

Electrode-potential measurements on plutonium[93] and uranium[94] chlorides have been made in fused chloride salts. The standard free energy of formation for solid plutonium trichloride from 958 to 1014°K is reported as $-221 + 0.05328T$ kcal/mole. The thermodynamics of reciprocal molten salt systems has been considered on a statistical-mechanical basis.[95] Thermodynamic properties of ruthenium chlorides were studied at temperatures of 650 to 1000°C and at chlorine pressures[96] of 0.1 to 1.5 atm. The important species in the vapor phase are the tri- and tetrachlorides.

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Section IV

WASTE DISPOSAL

Report of the NAS Committee on Disposal and Dispersal of Radioactive Wastes

In June 1956, the National Academy of Sciences published its first summary reports[1,2] of the findings and recommendations of six committees established to study the biological effects of atomic radiations. These committees cover the fields of genetics, pathology, meteorology, oceanography and fisheries, agriculture and food supplies, and the disposal and dispersal of radioactive wastes. The committees responsible for the first reports have prepared new summary reports[3,4] to bring the findings of the committees up to date. A general conclusion from the reports of all six committees is that the steady accumulation of scientific information since 1956 has not brought to light any facts that call for drastic revisions of their earlier recommendations. In the new reports the committees have in general devoted greater attention to future objectives in the study of biological hazards and to research programs that are needed to attain them. Highlights from the summary report of the Committee on Disposal and Dispersal of Radioactive Wastes are outlined below.

As of 1960, radioactive waste operations had not resulted in any significant effect on the public, its environment, or its natural resources. Extensive and continuing monitoring programs must be maintained to ensure a continuation of this status. Methods have been developed for the removal of major portions of the activity from many low-level radioactive wastes. Certain major AEC centers have been able to discharge safely directly to the environment large volumes of low-level wastes without treatment because of the type and quantity of radioactivity involved and the characteristics of the specific site environment. Existing treatment systems have satisfactorily handled intermediate-level radioactive wastes. Although it is generally agreed that tank storage is not an ultimate solution to the waste-disposal problem for high-level radioactive wastes, interim (2 to 10 years) tank storage will be an integral part of any final disposal system.

It is a general consensus that recovery from highly radioactive fuel-processing wastes of specific fission products such as Sr^{90}, Cs^{137}, and others would neither appreciably affect the waste-disposal problem nor significantly aid in its solution. The recovery of fission products would reduce the problem of heat dissipation in the residual wastes but would have little influence on the over-all safety or cost of waste control.

Solid wastes are presently disposed of by land burial at AEC sites or by burial at sea. With increasing waste volumes, and the geographic spread of the use of radioactive materials, permanent land burial sites are needed in various parts of the country.

The disposal of solid, packaged wastes into the ocean has been used in the United States for low-level-activity solid or packaged wastes. The safety of these operations has been supported by the views of experts in the marine sciences and other related fields, by the actual operating experience of the British in disposing of considerably greater quantities of liquid radioactive wastes to the Irish Sea, and by the preliminary but direct information from actual field studies made in both Atlantic and Pacific Ocean disposal areas.

Although limited U. S. data show the total cost for radioactive waste disposal to be high, it does not appear to be a limiting factor in the development of nuclear power. If economic power

from nuclear fission is not obtained, the failure to obtain it will not be due to the costs of waste management, which are approximately 3 to 5 per cent of the total plant cost.

Apparently, nothing inherent in the over-all waste-control problem should retard the development of the nuclear energy industry or, at the same time, interfere with adequate protection of the public health and safety. The types of potential waste-management problems that will require continued surveillance and supervision in the future in order to minimize exposure of man and his natural resources are (1) control and careful supervision of releases of low-level wastes in order to assure adequate protection of the environment, (2) possible leaching or relocation of small fractions of high-level wastes from underground storage sites, and (3) accidental irregular releases from nuclear energy operations.

Waste Packaging

In September 1959, Brookhaven National Laboratory (BNL) disposed at sea of some 1350 55-gal drums of radioactive wastes representing 15 months' accumulation.[5] The use of 55-gal drums for this purpose has now been discontinued because of the greatly increased concentrations and amounts of activity and the need to accommodate larger objects. Five types of reinforced-concrete vaults, weighing 10 tons when filled, have been developed and are now being used to package radioactive wastes (see Fig. IV-1). A preliminary cost study has indicated that the vault method will be considerably less expensive than the drum method for either sea or land disposal.

The new packaging method has been very successful in handling the increased volume of higher specific activity slurry (190 mc/gal)

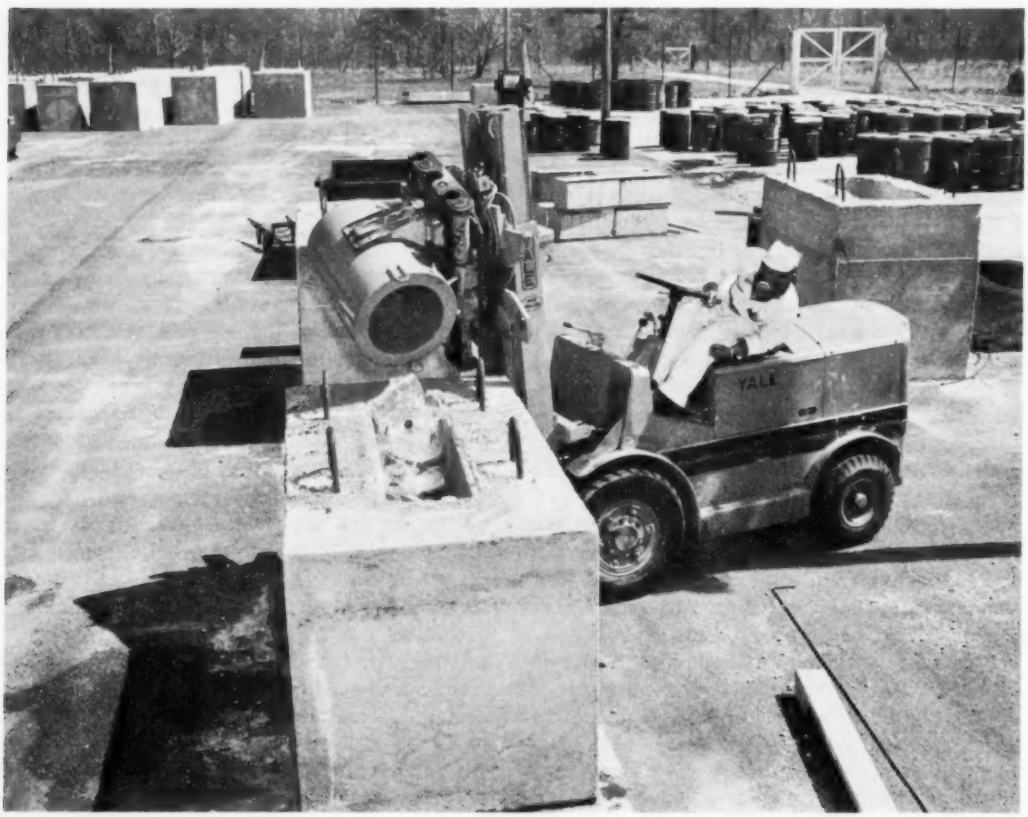

Fig. IV-1 Emptying highly radioactive waste from a lead container into a disposal vault with 17-in.-thick reinforced-concrete walls, for ultimate disposal by sea burial.

from the liquid-waste evaporation plant. This slurry is pumped into one of the concrete vaults and solidified with cement. The large block of solidified slurry is self-shielding to a considerable extent, and the 6-in. outer layer of clean concrete reduces the surface radiation level to about 200 mr/hr. About 20,000 gal/year is being packaged. One vault will hold an amount of slurry that formerly would have required 50 drums.

Low-Level-Activity Liquid Waste Treatment by Ion Exchange

A recent ORNL report[6] summarizes the laboratory-scale development of a phenolic-resin ion-exchange process[7] for the decontamination of large volumes of low-radioactivity-level process-water wastes. In this process the water is adjusted to 0.01*M* sodium hydroxide (*p*H slightly under 12), clarified to remove the small amount of solids, and passed through a bed of phenolic cation-exchange resin. When the water is made alkaline, more than half the radioactivity is removed by coprecipitation with the calcium and magnesium already present, and most of the remaining radioactivity is removed by the resin. The resin can be regenerated with 1*M* to 5*M* hydrochloric acid and the waste regenerant evaporated to one-half resin volume of concentrated radioactive waste to be stored, representing an over-all volume-reduction factor of 3000 to 4000 for the ion-exchange and evaporation steps. A small-scale pilot-plant demonstration of the phenolic ion-exchange process is planned to confirm these results under actual operating conditions. Preliminary drawings for the design of a 10 gal/min pilot plant have been issued.[8]

High-Level-Activity Liquid Waste Treatment and Storage

A Hanford report[9] summarizes the experimental studies that were conducted to evaluate the effectiveness of clinoptilolite for the removal of strontium and cesium from Purex-tank-farm and Redox-process condensate wastes. Progress on this work has been covered in previous Reviews.[10] Hanford has also reported on a heat-transfer design study[11] that defines the approximate temperature gradients which would exist across the walls of the Redox and the Purex type storage tanks for either uniform or incremental rates of temperature rise when the stored tank contents are heated (by fission-product decay) from ambient ground temperature (about 70°F) to boiling (about 230°F). Another study on the rate of heat loss from storage tanks to the ground was reported in an earlier Review.[12]

A cost study (to be published as report ORNL-3128) for interim liquid storage of high-activity wastes concludes that, with 4 per cent interest and the "present-worth" method of financing future capital outlays, the storage costs can range from about 0.002 mill/kw(e)-hr for 0.5-year storage to between 0.005 and 0.01 mill/kw(e)-hr for 30-year storage.[8]

An inorganic ion-exchange material, ammonium phosphomolybdate (APM), has been tested at ICPP because of its selectivity for cesium in the presence of ions such as sodium, potassium, aluminum, and hydrogen which normally interfere in an ion-exchange reaction.[7,13] A bed of APM supported on silica gel was shown to give a decontamination factor of approximately 3000 for Cs^{137} in aluminum nitrate–nitric acid solutions and a capacity of 35 mg of cesium per gram of APM. Wilding has summarized much of the work on this procedure in a topical report.[14]

Mercury cathode electrolysis is being studied at Idaho as a method for removing iron, nickel, and chromium from waste solutions resulting from processing stainless-steel reactor fuels.[7,14] It was demonstrated that up to 3 per cent iron or nickel could be electrolyzed into the mercury before the amalgam reached a semisolid state that would require treatment to remove the base metals. A maximum of 0.3 per cent chromium was taken up before electrolysis ceased and a fine black powder separated from the mercury. Faler and Anderson have discussed the separation of fission products from the iron, nickel, and chromium in this procedure.[15]

Reduction to Solids

A number of methods are being investigated for the conversion to solids of high-level-activity liquid wastes, including calcination, incorporation into glass, and fixation in ceramic sponges. Adsorption on mineral ion exchangers is being explored for the removal of cesium,

strontium, and plutonium from various waste streams. The AEC's research and development program for the handling and ultimate disposal of high-level-activity wastes was summarized in a paper presented at a Purdue University industrial waste conference.[16]

Calcination

ORNL continued its investigation of the effect of additives[8] for decreasing the volatility of ruthenium and sulfite during the pot-calcination treatment of high-level-activity wastes. Additions of phosphorous acid (H_3PO_3) to concentrations of 1.5*M* to 1.8*M* decreased the volatility of ruthenium to 0.02 to 0.03 per cent for two types of aqueous wastes. Smaller amounts of phosphorous acid (below 1*M*) were less effective in suppressing ruthenium volatilization during calcination. In a semicontinuous experiment with a Purex waste to which 1.5*M* phosphorous acid had been added, together with lesser amounts of calcium hydroxide, sodium hydroxide, and borax, the ruthenium volatilized was below the limit of detection (about 2 per cent for stable ruthenium).

The solid produced had a density of 2.6 g/cm^3, representing a solid-waste volume of about 6.1 gal per ton of uranium processed. In other experiments the calcined oxides from a Purex waste were incorporated into magnesium borophosphate glasses with softening points of about 850°C. These solids had densities of about 2.7 g/cm^3 and contained 38 to 54 per cent waste oxides, representing 4.8 to 6.9 gal of glass per ton of uranium processed.

Evans at the ICPP has summarized the operating experience with the 6-in.-diameter fluidized-bed pilot-plant calciner for aluminum nitrate-bearing wastes.[17] Pilot-plant studies in the 2-ft-square calciner have continued with investigation of the operating characteristics of one of the feed spray nozzles intended for use in the Demonstrational Waste Calcining Facility.[13] Runs of eight days' duration demonstrated that a feed rate for the liquid of at least 120 liters/hr through one spray nozzle could be maintained without inducing caking of the product or causing noticeable temperature fluctuations in the bed beyond a distance of 12 to 15 in. from the nozzle, measured along the axial center line of the spray pattern. At very low nozzle air-to-liquid volume ratios, particle growth increased, resulting in a bed of relatively large particles with poor heat transfer from the NaK tubes to the bed. Attrition of the calcined product was influenced to the greatest extent by the nozzle atomizing air (because of a high-velocity jet grinding action) and to a considerably smaller extent by fluidizing-air velocity and liquid-feed injection rates. Rapid erosion of the flat titanium nozzle face (0.86 in./year) during these tests led to the development of an extended cone tip, less susceptible to wear by impingement of alumina particles under the influence of an air vortex.

It was noted in a previous Review[7] that the physical structure of the alumina produced during operation of the fluidized-bed calciner has, for unknown reasons, rapidly shifted between an amorphous and a predominantly alpha crystalline structure.[7,13] The alpha content of the product affects its attrition rate and hence the product particle size and off-gas loadings; the absolute, and hence the bulk, density of the product is also affected by its alpha content.

Further study has been undertaken in an attempt to understand this phenomenon.[13] Examination of bulk product produced in the pilot plant, fines carried in the off-gas, and dissected particles (produced under both high and low alpha-alumina-forming conditions) demonstrated that in every case the fines elutriated from the calciner had a lower alpha-alumina content than the bulk product or any part of an individual dissected calcine particle. The data indicated that material which is either spray dried directly from the nozzle or attrited from freshly formed particle surfaces (and readily carried in the gas stream because of its small size) is predominantly amorphous, whereas that retained on calcine particles can either remain largely amorphous or be rapidly converted to the alpha form under conditions not yet understood. Preliminary laboratory investigations have led to partial conversion (5 to 65 per cent) of amorphous alumina to alpha alumina under influence of high temperature for prolonged periods (192 hr at 927°C), and more especially in the presence of relatively high concentrations of sodium nitrate and nitric acid, but have not yet resulted in significant conversion under the temperature conditions (400 to 500°C) prevailing in the calciner.

Ultrasonic coalescence[18] has been suggested by Aeroprojects, Inc., for the removal of radioactive particles (less than 1 μ in diameter) that are expected to remain in the off-gas from the

operation of the ICPP fluidized-bed calciner after the larger particles have been removed by conventional gas-cleaning equipment. Although ultrasonic forces can bring particles into contact with one another, they apparently cannot cause the particles to adhere. A concept successfully studied on a laboratory scale consisted of combining with ultrasonic coagulation the use of an additive liquid aerosol fog to the gas stream which improved ultrasonic coagulation and collection efficiency. By controlling gas-flow rate and additive-aerosol rate, this approach has been demonstrated to be capable of reducing simulant submicron solid aerosols to concentrations as low as 0.002 μg/cu ft. This was accomplished by using an intense planar ultrasonic standing wave and an additive liquid aerosol fog of 2- to 10-μ size which provides nuclei for agglomeration. Removal is partly effected by precipitation within the coalescence apparatus but must be completed by a collector, such as a cyclone type, that is effective for droplets with 3-μ and larger diameters.

Aeroprojects, Inc., is proposing that field tests with actual calciner reactor off-gases be made using a three-stage coalescence unit to determine the optimum conditions and performance with the radioactive particulate matter. Steam-driven whistles are expected to lead to operating economies, particularly if the condensate can be used as the additive aerosol. However, estimates for the scale of operation of the ICPP demonstration calciner indicate that 33 three-stage coalescence units are required and a 500-hp compressor is needed for operation of the ultrasonic generator whistles.

The ICPP is studying in the laboratory the calcination of fluoride-containing waste solutions[7,13] (e.g., from zirconium fuel processing). The process under consideration involves a precipitation step in which solid calcium oxide is used to neutralize the solution and precipitate the fluoride as calcium fluoride or zirconium and aluminum fluoride-containing compounds. The resulting slurry is then calcined. Laboratory data indicate that the optimum ranges of the reaction conditions for minimum volatilization of fluoride and minimum calcine leachability are (1) calcination temperature near 500°C, (2) calcium oxide-to-fluorine equivalency ratio of 0.75 to 1.0; aluminum concentration above 0.3M, and (3) nitrate concentrations either below 2M or above 3M. Preliminary laboratory research on the feasibility of the calcination of aqueous zirconium fluoride waste is summarized by Hickok and Madachy.[19]

One approach to the permanent disposal of highly radioactive wastes involves converting the waste to a granular solid and embedding the granules in a stable solid matrix having high thermal conductivity and low leachability.[10] An attempt to fix the activity in calcined alumina (containing Cs^{137}), by immersing the particles in molten aluminum and then cooling, resulted in a solid from which the activity was still leachable, although very slowly (40 per cent in 700 hr) as compared with the rate from uncoated alumina (70 per cent in 1 hr). In other experiments it was demonstrated that silica gel could be used to absorb a liquid waste and the waste calcined *in situ*. By repeated absorption-calcination cycles, a waste containing 2M aluminum nitrate was concentrated fivefold without plugging the pores between the silica-gel granules, which were then embedded in a metal matrix. The absorption of synthetic liquid waste by silica gel provides a method of progressing from a high-specific-activity liquid waste to a granular solid suitable for fixation in metal with a minimum of handling of the liquid and solid.[13]

Adsorption on Natural Materials

A Hanford study of the possible application of Florida pebble phosphate rock for plutonium recovery[7] from a building sump waste was continued.[20] It was found that, upon standing, the plutonium removed by the mineral gradually becomes unavailable for elution, apparently by means of solid-state diffusion along crystal interfaces. Freshly loaded phosphate rock may be eluted with a solution of sodium carbonate, which replaces the outer layer of phosphate mineral with calcite, thus releasing the plutonium remaining near the grain surface. When not eluted, the phosphate automatically recovers plutonium adsorption capacity upon standing. Canadian apatite mineral, which has the same composition but a different crystal structure, was found to have a much lower plutonium capacity than the Florida pebble phosphate with no improvement in elution performance. For complete recovery of plutonium, the Florida pebble phosphate can be dissolved in four bed volumes of 6M nitric acid (except for about 2.5 per cent insoluble silica).

In laboratory experiments[20] with this sump waste solution, a bed of the Florida pebble phos-

phate was cycled three times through a loading, eluting, and recharging cycle. The capacity of the bed to 10 per cent plutonium breakthrough increased with each cycle, being 210 bed volumes for the first, 425 bed volumes for the second, and 600 bed volumes for the third. Prompt elution after the first cycle recovered 95 per cent of the plutonium. The bed was permitted to stand for two days before elution after the second and third loading cycles, and as a result elution recovered only about 10 per cent of the plutonium on the bed. Elution was performed with five bed volumes of 1*M* sodium carbonate solution. The mineral was then recharged with five bed volumes of 0.2*M* trisodium phosphate solution.

Conversion to Glasses

The Massachusetts Institute of Technology has been studying the incorporation, into a vitreous medium, of the high-level-activity wastes resulting from the processing of various types of spent fuel elements. Their study on the conversion to vitreous fusions of aluminum-bearing fission-product wastes was described in an earlier Review.[7] This approach has also been investigated for fission-product wastes from the processing of zirconium-clad fuel elements.[21] A powdered calcined oxide synthetic waste, obtained from BNL, was used in this investigation. The vitreous mixes were produced using individual components of glass and naturally occurring igneous materials and industrial slag wastes.

On the basis of the studies conducted, it was concluded that stable glasses can be prepared from calcined zirconium wastes mixed with calcium oxide (CaO), silicon dioxide (SiO_2), and aluminum oxide (Al_2O_3) with up to 15 per cent of wastes in the glasses. Stable glasses can also be prepared from igneous rocks and industrial slags mixed with calcined zirconium wastes and fired to fusion temperature. More than 15 per cent of calcined waste cannot be incorporated in a glassy medium obtained from the naturally occurring materials investigated. The corrosion rates obtained from glasses prepared with naturally occurring materials such as igneous rocks have the same order of magnitude as those obtained from relatively pure components. Increasing the lime content of the glass produces a decrease in Cs^{137} volatilization during firing.

Absorption and Fixation in Porous Ceramic Sponges

The Coors Porcelain Company, Colorado, and the Los Alamos Scientific Laboratory (LASL), New Mexico, are participating in a joint study to investigate the absorption of liquid radioactive waste in ceramic sponges which could be dried and fired, thus permanently fixing the radionuclides in the ceramic material.[16,22]

Briefly, the process involves the preparation of a highly porous clay body which is fired to about 1100°C. This body is then soaked in the liquid waste, dried, and resoaked. The cycle is repeated as many as five times. Finally, the clay body is fired at 1300°C to fix the radionuclides permanently.

A ceramic sponge utilized for this application should have the following characteristics: (1) be made from inexpensive, readily available ceramic raw materials, (2) be fabricated inexpensively, (3) initial sintering should be accomplished in the temperature range 900 to 1150°C, (4) the sintered sponge should have a porosity (the open-pore volume of a solid expressed as a percentage of its total volume) of at least 40 per cent and preferably 50 to 70 per cent, (5) sponge pore structure must be fine and homogeneously distributed, (6) the sintered sponge must withstand repeated immersion in radioactive waste solutions without dissolving or slaking, (7) a high retention of waste salts and radionuclides in the dried sponge which, on firing at temperatures around 1200°C, will completely vitrify, resulting in a body with near zero porosity, (8) the vitrified sponge must not disintegrate or be affected by radiation damage, and (9) the final fired sponge must be sufficiently rugged to withstand normal handling without shattering or chipping prior to final disposal.

Spherical sponges were chosen for the process for the following reasons: (1) chipping of edges and corners of vitrified radioactive sponges is undesirable, (2) in storage there would be a guaranteed void volume in the mass to allow circulation of cooling air, and (3) spheres offer a minimum surface for maximum volume, which is important in minimizing leaching. In determining the optimum size of balls to be used, considerations such as the time required to saturate the balls per unit volume were taken into account. Based on these considerations, a 2-in.-diameter ball appears

to be the most economical to produce in large quantities. Of 35 three-component ceramic systems selected for vitrification studies, only three compositions (with varying percentages of diatomaceous earth, kaolin, and feldspar or nepheline syenite) had the desirable combinations of firing and fired properties which make them worthy of further consideration. A 10 gal/day pilot plant is to be installed at LASL in 1961 and operated with tracer amounts of radioactivity in simulated waste.[16]

Final Disposal Methods

Ground Disposal

At ORNL, seepage pits[7] constructed in a Conasauga shale formation have been used for the disposal of intermediate-level-activity liquid waste, essentially a basic sodium nitrate solution with Cs^{137} contributing the majority of the activity. The performance of the seepage pits under field conditions is influenced by factors of porosity, permeability and hydraulic gradients, and the partial capacity of the Conasauga shale for the sorption and retention of the radioactive constituents in the waste. A detailed study[23] of the retention of cesium by Conasauga shale has shown it to be effective for removal of cesium from the waste stream. The partial cesium capacity of the shale was found to be dependent on the nature and concentration of the major stable cations present in the waste. The capacity of the shale for "fixation" of cesium greatly exceeds the capacity of the shale for sorption of cesium from the waste stream. The cesium thus retained from the waste stream would be very difficult to remove from the formation by percolating ground water, and any cesium leached would be resorbed from the leaching solution when unsaturated shale was contacted because of the high affinity of the shale for cesium. Thus, if the pits are removed from operation before complete saturation of the formation is accomplished, there would seem to be little danger of cesium transport due to leaching processes.

Disposal into Salt Formations

The possibility of disposing of radioactive wastes in cavities in natural rock salt formations is being investigated at ORNL.[10,16] As part of this program, the effects of radiation (cumulative doses ranging from 1×10^6 to 5×10^8 r) and temperature (room temperature and 200°C) on the physical properties of aggregates of natural rock salt crystals were studied.[24] It was concluded that radiation effects on the physical properties of rock salt will not prohibit the disposal of radioactive wastes in salt cavities. Within the statistical variation of the experiment, radiation causes only minor changes in the physical properties of rock salt. Apparently, any effect radiation may have on the physical properties of rock salt is small and becomes apparent only at the higher doses.

As expected, the plasticity of rock salt increases quite rapidly with temperature. The compressive strength, modulus of elasticity, yield strength, and apparent elastic limit are less at 200°C than at room temperature.

Disposal into Porous Strata of Deep Wells

ORNL and the U. S. Bureau of Mines are carrying out laboratory investigations and theoretical studies into the feasibility of disposing of high-level-activity waste solutions by injecting them into deep (several thousand feet) porous formations.[16]

In conjunction with the above studies, the U. S. Geological Survey is compiling detailed information on deep sedimentary basins in the United States to determine which areas may be feasible for a field-scale experiment on this waste-disposal approach. Summary reports[16] have been completed on the distribution and general nature of sedimentary basins in the United States, including the San Juan Basin of Colorado, Utah, and New Mexico,[25] the Central Valley Basin of California, and the Appalachian and Michigan Basins. These reports summarize stratigraphy, with emphasis on the lithologic (rock) characteristics and general structural features.

Separation of Specific Isotopes

Purified multiliter quantities of Kr^{85} and of xenon are being recovered from fission-product gases from spent-uranium-fuel dissolutions at ORNL.[26] An adsorption process is used which is based on a combined procedure of selective adsorption of the desired gases on activated coconut charcoal followed by elution with a carrier gas (helium). The chemical and radiochemical purities of the krypton product are

greater than 99 per cent and essentially 100 per cent, respectively. The xenon-product purity is greater than 98 per cent.

ORNL is continuing its investigation of a head-end precipitation step for strontium in Purex type wastes prior to its recovery on an ion-exchange column.[7] The precipitation is to take place in an 85 per cent nitrate-ion medium. Recent laboratory data[8] have shown that the amount of precipitated strontium increased as the waste was diluted with increasing amounts of fuming nitric acid, from about 10 per cent at about 60 per cent nitric acid to almost 90 per cent at about 80 per cent nitric acid. More than 50 per cent of the iron and 5 to 10 per cent of the aluminum, the chief cationic impurities in the waste, precipitated as sulfates with the strontium product in the nitric acid concentration range tested.

The results of a Savannah River development study,[27] based on Hanford work, have shown the precipitation of the rare-earth fission products as double sulfates to be a satisfactory primary step in their recovery from Savannah River's Purex-process high-activity-waste concentrate (HAWC). The method recovers about 90 per cent of the desired rare earths, concentrated from the Purex waste by a factor of 200 and moderately well separated from other fission products. This concentrate is considered suitable for storage prior to recovery of individual rare earths, such as Pm^{147}. The procedure developed involves (1) adjustment of the waste solution to 1.5*M* sulfate with sulfuric acid and neutralization to about 0.5*M* hydrogen ion with sodium hydroxide, (2) digestion at 70°C for 3 hr, (3) separation of the double-sulfate crystals by centrifugation, (4) conversion of the rare-earth double sulfate to hydroxide by heating the crystals with sodium hydroxide solution, and (5) dissolution of the rare-earth hydroxide in nitric acid.

Radiation Applications, Inc., in an analysis of radiation processing with fission-product beta emitters, has shown that there are promising areas of commercial application for beta-radiation sources.[28] In general, these are applications that require low penetration, low dose, and low production rates. Under these conditions, they believe that beta sources stand a good chance of being an economically attractive energy source and can compete with current machine-electron prices at the 1-kw level if the costs of fission products decrease to the 20 cent/curie level. Their calculations indicate that, on a cost-per-unit-energy basis, Sr^{90} is by far the most economical of the nuclides considered for use in beta sources. Other aspects summarized in this report include a study of fabrication technology of beta sources, calculations of the dosage and beta-utilization efficiency associated with source-absorber configurations of industrial interest, an analysis of the potential applications, an engineering cost analysis of beta power, and recommendations for future work.

The recovery and purification of Sr^{90} from Purex-plant wastes by solvent extraction and ion-exchange processes are under continuing study at Hanford. A flow sheet, employing pulse-column solvent extraction for the recovery of megacurie quantities of strontium, is being developed in the laboratory and in the pilot plant.[29,30] Two extraction-strip cycles are planned in which the required degree of separation and purification of strontium from the other constituents is obtained by controlling the *p*H. A flow sheet (described in a previous Review[7]), which is being tested in the laboratory and is currently considered optimum, specifies a first column feed with a *p*H of 4.7 and containing sodium acetate and EDTA (ethylene diamine tetraacetic acid) for buffering and for complexing. The scrub solution is 0.6*M* citric acid, and the extractant solution is 0.4*M* D2EHPA (di-2-ethylhexyl phosphoric acid)–0.2*M* TBP–Shell E-2342 diluent. Good strontium recovery (>95 per cent) was obtained in runs with tracer- and high-level-activity feeds. Cerium, ruthenium, and zirconium-niobium decontamination factors of about 20 to 75, 200 to 1000, and 1500 to 3000, respectively, were obtained. In the second column, 1.0*M* citric acid is used to strip strontium from the first-column product stream. Strontium recovery in a high-level-activity run was poor (about 60 per cent), possibly due to difficulty in maintaining proper flows.[30] Tracer studies indicate strontium recovery of 95 per cent or better should be obtained. Cerium decontamination factors of about 50 were obtained.

Two more runs[29,30] for purification of Sr^{90} have been made at Hanford utilizing an ion-exchange process.[7] High concentrations of ammonium and sodium ions in fresh feed solutions[20] were found to reduce the strontium capacity of ion-exchange columns and cause premature breakthrough of the strontium. The sodium ion is already present in the as-received

Sr^{90} Purex-plant concentrate, and the ammonium ion comes from the ammonia added to neutralize the nitric acid used to dissolve the solids present in the crude. Simple dilution of the feed seems to overcome this effect, the degree of dilution giving an almost proportionate increase in capacity. The Sr^{90} product can be eluted either with 5*M* ammonium nitrate (which is somewhat superior to nitric acid) or with HEDTA (*N*-hydroxyethyl ethylene diamine triacetic acid). For storage purposes the ammonium nitrate solutions are more stable, since HEDTA solutions undergo radiolysis. For maximum loading of strontium on Decalso,[10] an inorganic ion-exchange material, HEDTA is the preferred eluting agent. Aluminum contamination in rework material was found to absorb preferentially and to serve as a barrier to cerium and rare earths when aluminum-free feed was introduced. The aluminum and absorbed cerium and rare earths were successfully removed with an HEDTA wash.

Solids present in feed solutions can cause difficulties during the ion-exchange loading cycle. Centrifugation is being used to clarify the feed solutions.[29,30]

Chemical means of dissolving expended ion-exchange resin (Dowex 50 X-12) were studied.[30] It is desirable to destroy the ion exchanger before discarding it to underground waste tanks because of possible lowering of the *p*H of the waste (with consequent increased corrosion of the tank) during radiolytic decomposition of the resin. The two solutions studied, nitric acid–manganous ion [HNO_3-Mn(II)] and potassium permanganate, will solubilize the resin, the reaction with HNO_3-Mn(II) being somewhat easier to control.

For off-site shipment of Sr^{90} and Ce^{144}, Hanford is currently investigating the evaporation and calcination of Sr^{90} solutions in small cylindrical vessels or canisters ($1\frac{1}{2}$- to 2-in.-diameter pipe 9 in. long) that can also be used as the shipping container.[20,28] The calcined strontium oxide is dense, hard, and adheres tightly to the vessel. It can be disintegrated to a crumbly powder by reacting with steam at 150 to 200°C, forming strontium hydroxide [$Sr(OH)_2$]. For a 2-in.-diameter canister, the practical maximum of material that can be handled at one time is approximately 500 g of strontium oxide (30,000 curies).

Cerium oxalate (solid) can be easily calcined to cerium oxide in a shipping-canister calciner by heating[29] above 350°C. The product has a tap density of 1 g/cm^3 and is probably a mixture of cerous oxide (Ce_2O_3) and ceric oxide (CeO_2). To prevent pressurization of shipping containers, it will be necessary to halt the decomposition at cerous oxide. Ceric oxide would produce oxygen as the Ce(IV) decomposes to form trivalent oxide.

Smith at Hanford[31] has discussed the design and hazard evaluation of a lead-shielded cask for off-site shipping of Ce^{144}. It was designed for nominal shipments of 5×10^5 curies of Ce^{144} (with associated impurities, the total contained activity is about 8×10^5 curies). Shipment of large quantities of Sr^{90} or the rare earths appears feasible in this cask, provided that the shielding and heat-dissipation design criteria are not exceeded.

To evaluate the hazards involved in shipping casks of Ce^{137} adsorbed on a synthetic zeolite, cesium leaching and volatilization studies were conducted.[30] The laboratory beds contained 12 mc of Cs^{137} per gram of zeolite, the cesium coming from a Purex-waste-tank supernatant solution. Simulating an immersion of the cask in the Missouri River, leaching with 20 bed volumes of synthetic river water (about 9 meq of cation per liter), only removed some 0.6 per cent of the cesium from the loaded zeolite. To simulate a high-temperature incident, the amount of cesium volatilized in 2 hr was determined at temperatures of 1350 and 1500°C in atmospheres of air and of helium. The amount released in either atmosphere ranged from about 0.3 to 0.7 per cent of the cesium loaded on the zeolite. Cesium was not released below 1200 to 1300°C, near the fusion temperature of the zeolite.

Clinoptilolite would reduce the risk of accidental spills en route if used as a carrier for radiocesium, its capacity for cesium being more than 2.5 times that of a synthetic zeolite. A leaching comparison was even more favorable, with synthetic river water removing only one-tenth as much cesium from clinoptilolite per volume of leach water passed through.

The final report (described in a previous Review[32]) by Radiation Applications, Inc., on the application of a foam separation process[33] for the removal of strontium and cesium from Purex type waste streams has been reissued[34] with a new title and report number. Also available is literature that describes the separation

and purification of Pa^{231} by an ion-exchange technique.[35]

Other Literature

Recent research and development studies on radioactive waste management being carried out by the AEC and its contractors are described[36] in the AEC's annual report to Congress for 1960. Highlight summaries of programs covered include environmental studies on wastes, sea disposal, the handling and treatment of low-, intermediate-, and high-level-activity liquid wastes, and gas effluent studies. The Commission's policy for land disposal of low-level-activity packaged radioactive waste is summarized.

Two new books have recently become available which cover the handling and treatment of radioactive wastes.[37,38] In each book the editors and their contributing authors have provided a broad coverage of the field. One can find information on current operating practices, experimental data, equipment, process and treatment development, fission-product separation and their use in research and commercial applications, and economic and legal aspects of waste disposal. These publications should prove to be useful as reference books to those interested in familiarizing themselves with the field and to those seeking additional background information.

Two of the invited papers on radioactive waste management and disposal presented at the 1960 Winter Meeting of the American Nuclear Society[10] are available as separate reports. One describes the radioactive waste management program at the Savannah River Plant;[39] the other describes the pot calcination process for converting high-activity waste to solids for permanent disposal.[40]

An English translation[41] is available of three published Japanese articles dealing with liquid entrainment in evaporation processes.

The Air Cleaning Laboratory of the Harvard School of Public Health conducts research and development on air- and gas-cleaning devices and methods for their testing and evaluation.[42] In their progress report,[43] results are given for performance tests of various filters: (1) a commercial bag collector that is continuously cleaned by counterflow pulses of high-pressure air, (2) a Dynel fiber filter for the filtration of sodium-potassium alloy (NaK) fume, (3) a slag wool-fiber filter for the cleanup of particulate material in the off-gas of an institutional type incinerator, (4) miscellaneous media for the collection or removal of radioactive iodine, and (5) water-jet scrubbers.

Burning tests of high-efficiency filters (CWS-6 type) of various kinds of construction were conducted by the Dow Chemical Company, Rocky Flats Plant, Colorado.[44] Studies were made of flame propagation, fire-alarm systems, effectiveness of water sprays, and fire-fighting techniques. Some conclusions from this report are as follows: A smoke alarm performed best of four fire-alarm systems evaluated. Fog type water sprays were found to be very effective in controlling fires in the initial stages of burning and appeared to be as effective in the advanced stages of a fire. The flammability of filters with a cellulose-asbestos medium was reduced to nearly that of the noncombustible types by substituting aluminum for the paper separators used to support the filter medium.

In nuclear fuel solvent-extraction processes in which nitric acid is used as a salting agent, its recovery is important because of the large savings gained from the reuse of the acid and the reduction in waste-storage costs. The recovery of uncontaminated nitric acid from nitric acid solutions of fission products, however, is hampered by the volatilization of ruthenium. Wilson[45] has reported the results of laboratory experiments at Hanford designed both to examine some chemical factors that would enhance ruthenium volatilization and to define distillation conditions that would suppress its volatilization.

The Armour Research Foundation has issued a final report[46] summarizing its program in development of methods for scavenging radioactive particles that might be released to the air or in the ocean by the reactor system of a nuclear-powered ship.

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Section V

PRODUCTION OF URANIUM, THORIUM, PLUTONIUM, AND THEIR COMPOUNDS

Uranium Trioxide Production

Production by Continuous Method

The conventional method of producing uranium trioxide is by batchwise calcination of uranyl nitrate in agitated reactors (denitration pots). This method has several disadvantages, chief of which are a high incidence of pot failures (caused by excessive heating and thermal cycling) and variability of the oxide product. These disadvantages led to the development at Fernald of a continuous-pot denitration system that has proved capable of sustained operation at production rates greater than those obtained in the batch process.[1] During operation of the continuous-pot denitrator, it was observed that an increase of the ammonia content of the uranyl nitrate feed solution produced crystals of ammonium uranyl trinitrate which necessitated occasional shutdown of the denitrator. The ammonia content of uranyl nitrate feed must be kept below 15,000 ppm (uranium basis) to prevent crystallization at the normal feed density of 2.5 g/ml. Since ammonium uranyl trinitrate decomposes without going through a dough stage, tests[2,3] were made to evaluate the properties of uranium trioxide prepared from this material. Operation of the continuous pot can be maintained on a sustained basis[2] with feed containing 15,000 to 19,000 ppm ammonia provided that the feed density is kept at 2.4 g/ml. Close supervision of the feed density is necessary since the density gradually increases with time.

Denitration of ammonium uranyl trinitrate yields a light, finely divided form of gamma-uranium trioxide.[3] This oxide exhibited a surface area higher than that of conventional (batch-produced) uranium trioxide. However, the activity of the oxide in reduction and hydrofluorination, as measured in standard laboratory tests, was slightly less than that exhibited by production oxide.

Properties of Uranium Trioxide

Production-grade uranium trioxide containing 700 ppm sulfate is reduced to uranium dioxide more rapidly as the particle size is decreased.[4] The increased reduction rate is attributed to the larger surface area and lower U_3O_8 content of the smaller particles. Grinding the larger uranium trioxide particles to less than 100-mesh size improves over-all reactivity.

Investigations made at Mallinckrodt's Weldon Spring Plant[4] of highly sulfated pot-denitrated uranium trioxide indicate that hydrofluorination time is decreased with increasing sulfate content to a level of 3700 ppm sulfate. A greater increase in sulfate results in a decrease in hydrofluorination rate. The activation of the uranium dioxide by sulfate is predominantly due to an increased surface area.

Metallic impurities (iron, nickel, molybdenum, and vanadium) appear to be concentrated in the coarse particles. The AOI (ammonium oxalate insolubles) and water solubles also are not uniformly distributed in the green salt.[4]

Ondrejcin and Garrett have reported on the kinetics of the thermal decomposition of both anhydrous uranyl nitrate and uranyl nitrate dihydrate.[5] At temperatures from 250 to 450°C, the thermal decomposition of anhydrous uranyl nitrate *in vacuo* follows first-order kinetics to yield an amorphous uranium trioxide as the only nonvolatile product. The thermal decomposition of uranyl nitrate dihydrate occurs as two independent reactions following first-order kinetics: dehydration to form anhydrous uranyl nitrate and denitration to uranium trioxide. Uranyl hydroxynitrate $[UO_2(OH)NO_3]$ was ob-

served as an intermediate in the decomposition reaction. At atmospheric pressure between 250 and 400°C, uranyl nitrate dihydrate decomposes to give gamma-uranium trioxide. Both gamma- and beta-uranium trioxide are produced at 500°C. Vacuum denitration of uranyl nitrate dihydrate produces an amorphous allotrope of uranium trioxide. Observations on the thermal decomposition of uranyl carbonates also have been reported.[6]

The infrared spectra and structures of some hydrated uranium trioxides and ammonium diuranates have been published.[7] It appears that the structure of ammonium diuranate is in the form $UO_2(OH)_2xNH_3yH_2O$, although materials prepared by various means may contain an excess or deficiency in either water or ammonia content.

Preparation of Fuel-Grade Uranium Dioxide

Conversion of Uranium Hexafluoride to Uranium Dioxide

The conversion of uranium hexafluoride to uranium dioxide by direct reaction with steam and hydrogen is being investigated at ANL[8,9] as a means for lowering the cost of producing reactor-grade oxide for ceramic fuels. Uranium hexafluoride is reacted with steam at 225°C to form uranyl fluoride in a fluid-bed reactor. Uranyl fluoride is then reduced to uranium dioxide with a hydrogen-steam gas mixture. The reactions have been carried out simultaneously in a single reactor,[10] but work is now being concentrated on the two-step procedure because of greater flexibility in choice of reactor conditions and process control.

The process variables of the uranium hexafluoride–steam reaction have been studied in a 3-in.-diameter Monel reactor with uranium feed rates up to 174 lb/(hr)(sq ft of reactor cross section). The major problem associated with this process step is the continuous formation of fine particles that eventually affect bed fluidity. Proper sizing of starting beds (average particle diameter of 250 μ or less) assures particle growth; however, continuous operation requires a seed-particle feed stream at a rate equivalent to 16 per cent of the uranium hexafluoride rate to maintain bed fluidity. Regulation of the rate of seed-particle addition to offset growth without entering the region of fines formation (average bed diameter less than 250 μ) has not been successful owing to the continuous formation of small amounts of fines partially offsetting seed-particle requirements. The operation of the reactor with a separate filter section in which the fine particles would be collected separately and not returned to the bed is being evaluated. This modification should tend to stabilize any variation in the average particle size during operation of the reactor.

The reduction of uranyl fluoride to uranium dioxide has been studied in batch fluidization runs in a 3-in.-diameter fluid-bed reactor.[8,9] A mixed gas of steam and hydrogen gas gave much faster conversion than hydrogen alone. A typical product from a 3-kg batch run contained 210 ppm residual fluoride, which is considered suitable for reactor-fuel-grade oxide. This material was prepared in 5 hr at 650°C using a gas stream of 3 parts hydrogen and 1 part steam.

Uranium dioxide has also been prepared from uranium hexafluoride gas by aqueous methods. At the Oak Ridge Y-12 Plant,[11] uranium hexafluoride was vaporized and dissolved continuously in water to form a solution of uranyl fluoride. A special orifice nozzle was designed to provide instantaneous hydrolysis without the formation of uranyl fluoride crystals. Uranium dioxide was prepared through a sequence of operations involving precipitation and calcination of ammonium diuranate followed by reduction to uranium dioxide. The final oxide powder, containing approximately 1000 ppm fluoride, sintered to a high density (> 94 per cent of theoretical) at 1750°C. A review[12] of methods for producing free-flowing uranium dioxide powders with dense particles less than 10 μ in size has been published.

Coating of Uranium Dioxide Particles

The coating of individual uranium or uranium dioxide particles with a strong, uniform, corrosion-resistant, impervious metallic coating has been demonstrated using reduction of volatile halides and vapor-deposition techniques.[13] In the case of uranium dioxide spheres used in nuclear fuels, the coating can act as barrier against the interaction of the oxide with reactive matrices and inhibit the diffusion of fission products into the matrix. In addition, the metallic coating improves the over-all

thermal conductivity of a consolidated mass of ceramic particles by providing a continuous metallic, heat-conducting network to the surface of the element.

Procedures were developed[13] for depositing, on individual uranium dioxide particles, continuous metallic coatings of niobium, chromium, molybdenum, vanadium, silicon, and niobium-5V alloy metals by the reduction of the volatile metal chlorides with hydrogen. Process conditions were established in vibrating-pan reactors using 1-lb batches of 100- to 140-mesh uranium dioxide particles. The reduction of chromic chloride with hydrogen did not produce suitable metal deposits owing to attack on the uranium dioxide by the chlorine evolved in the thermal decomposition of the chloride. Sound coatings were obtained, however, if the uranium dioxide particles were precoated with a thin layer of nickel or niobium. Nonporous chromium deposits were obtained on uncoated uranium dioxide particles by the pyrolysis of chromium dicumene at 425°C and by vapor plating of chromium metal under high vacuum. Coating procedures involving displacement of electrolytic methods were investigated for applying metal deposits on uranium metal.

The encapsulation of individual uranium dioxide particles with ceramic coatings by fluidized-bed techniques has been demonstrated at BMI.[14] Alumina coatings can be deposited on uranium dioxide particles by hydrolysis of aluminum chloride vapor at temperatures of approximately 1000°C. Recent work[15] indicates that between 900 and 1150°C the coating temperature variable is quite critical in relation to the type of coating deposited. At 900°C a frosty, translucent-to-opaque coating is obtained, whereas at a temperature of 1150°C a transparent coating is deposited. The degree of crystallization of the alumina appears to increase with deposition temperature. Both alumina- and carbon-coated uranium dioxide particles are being evaluated for fission-product retention by in-pile tests.

Uranium Tetrafluoride Production

Fluid-Bed Operation

Since fluid-bed reactors offer efficient gas-solid contact and temperature control, considerable attention has been directed toward employing fluid-bed reactors in the preparation of uranium tetrafluoride. The application of fluid-bed techniques in the processing of enriched uranium tetrafluoride has been studied in some detail by Levey at the Oak Ridge Y-12 Plant.[16] Steady-state operation[17] of a two-stage fluid-bed hydrofluorinator at Weldon Spring has produced uranium tetrafluoride with an average assay exceeding 98 per cent at a rate of 50 lb/hr. Uranium dioxide is continuously fed to the first stage and contacted with recycle hydrogen fluoride (approximately 55 per cent in steam) at a bed temperature of 320°C. The intermediate product (70 per cent uranium tetrafluoride) is converted to uranium tetrafluoride in a second stage employing an internal tapered mandrel. Bed temperatures from 425°C at the top to 600°C at the bottom of the reactor were used, with anhydrous hydrogen fluoride as the reactant gas. The function of the internal tapered mandrel[14] is to minimize gross mixing of the solids. The two-stage reactor has been demonstrated under conditions simulating the use of 1.05 times theoretical anhydrous hydrogen fluoride with azeotrope recycle.

Preparation from Ammonium Diuranate

A method of preparing uranium tetrafluoride directly from ammonium diuranate is the subject of a recent patent.[18] Gaseous ammonium fluoride or ammonium bifluoride is passed over ammonium diuranate in a reactor at 500 to 700°C for 1 to 2 hr. The reaction proceeds as

$$3(NH_4)_2U_2O_7 + 24NH_4F \rightarrow 6UF_4 + 21H_2O + 2N_2 + 26NH_3$$

The gaseous products may be treated to recover ammonia and excess ammonium fluoride. Conversion to uranium tetrafluoride is said to be 99 per cent.

Factors Influencing Quality of Green Salt

Uranium tetrafluoride is produced from uranium trioxide by gas-solid reactions involving reduction with hydrogen to uranium dioxide followed by hydrofluorination to uranium tetrafluoride. The quality of the green salt is greatly affected by variables in the denitration process, sintering of intermediate oxides, presence of impurities such as sodium, and the use of additives such as sulfate. A comprehensive study of the factors that affect green-salt

quality has been made in laboratory tests.[3,4] The hydrofluorination rate of uranium dioxide can be substantially increased by intermediate oxidation of the initial uranium dioxide followed by rereduction.[3] The optimum temperatures for the initial reduction, oxidation, rereduction, and hydrofluorination were found to be 595, 400, 540, and 540°C, respectively. Increasing the oxidation and hydrofluorination temperatures above these values had a detrimental effect on the hydrofluorination rate, whereas increasing the initial reduction or rereduction temperatures by about 57°C had no significant effect. Partial oxidation of the initial uranium dioxide followed by complete rereduction was found not to be effective as compared with complete oxidation.

Fluorinating Agents for Uranium Hexafluoride

Sulfur tetrafluoride has been shown[19] to be a good fluorinating agent for uranium oxides and oxyfluorides. The reaction of sulfur tetrafluoride with uranium trioxide and uranyl fluoride at 300°C produced uranium hexafluoride and thionyl fluoride in both cases. Both uranium tetrafluoride and uranium hexafluoride were identified as products in the reaction between uranosic oxide (U_3O_8) and sulfur tetrafluoride. In 1 hr at 500°C, an 85.5 per cent conversion of uranium dioxide to uranium tetrafluoride was found. No reaction was observed at 350°C. Under no circumstances does sulfur tetrafluoride act as an oxidizing agent in these systems.

The kinetics and mechanism of the reactions between sulfur tetrafluoride, uranium trioxide, and uranyl fluoride have been studied at ANL.[9] In considering the total reaction of uranium trioxide with sulfur tetrafluoride, the following mechanism was suggested:

$$UO_3 + SF_4 \rightarrow UO_2F_2 + SOF_2$$

$$UO_2F_2 + SF_4 \rightarrow UOF_4 + SOF_2$$

$$UOF_4 + SF_4 \rightarrow UF_6 + SOF_2$$

The first step in this mechanism was confirmed by chemical and X-ray-diffraction analyses. In no case was the formation of UOF_4 observed; its existence as a reaction intermediate is inferred by considering steric effects on the reaction. An activation energy of 32.4 kcal/mole for the reaction of uranyl fluoride with sulfur tetrafluoride was calculated from experimental data.

The production of uranium hexafluoride directly from uranium trioxide with sulfur tetrafluoride was studied[9] in an exploratory experiment carried out in a 2-in.-diameter fluid-bed reactor. The over-all reaction may be represented as $UO_3 + 3SF_4 \rightarrow UF_6 + 3SOF_2$. Uranium hexafluoride production rates of 22 and 66 lb/(hr)(sq ft of reactor area) were achieved at temperatures near 400°C using concentrations of sulfur tetrafluoride in nitrogen of 25 and 44 per cent, respectively. A reactant gas efficiency based on uranium hexafluoride production of 43.5 per cent occurred at the high sulfur tetrafluoride concentration. No attempt was made to optimize process conditions; however, improved production rates would be achieved using higher sulfur tetrafluoride concentrations. The success of this single demonstration test suggests that this reaction might be considered as an alternate for feed-materials production if sulfur tetrafluoride could be made at very low cost.

The reaction between uranyl fluoride and chlorine trifluoride to produce uranium hexafluoride has been studied[20] in the temperature range of 50 to 150°C. The reaction proceeds to completion in the temperature range studied with the gaseous reaction products being, in addition to uranium hexafluoride, oxygen, chlorine monofluoride, and chlorylfluoride. It was observed that the initial reaction of residual water of hydration in uranyl fluoride with chlorine trifluoride is very rapid compared with the subsequent process producing uranium hexafluoride.

Preparation of Uranium Carbides

At the present time, the AEC's Division of Reactor Development is supporting several programs intended to develop and evaluate bulk uranium carbide as fuels. To coordinate the efforts of the various laboratories engaged in research on carbide fuels (15 laboratories have AEC contracts), a series of informal meetings has been held to exchange information and plans. The proceedings of the December 1960 meeting held at ORNL have been published.[21] Considerable information is presented on the methods for preparing uranium

monocarbide, physical and chemical properties of cast and sintered forms, and radiation effects. A summary of fuels and materials development during 1960, which includes a review of uranium carbide technology, has been issued.[22]

Pyrolytic carbon coatings have been applied to uranium monocarbide and dicarbide particles by the decomposition of hydrocarbons in both tumbling-bed and fluid-bed reactors.[15] Successful carbon coatings were applied to uranium dicarbide spheres in a fluidized bed at 1400°C. The particles from two separate tests showed both laminar and columnar structure in the coatings. Nonuniform coatings were obtained in the tumbling-bed reactor at temperatures between 1500 and 1750°C. Results have indicated that both the coating temperature and deposition rate affect the occurrence of either an apparent laminar or columnar structure in the pyrolytic carbon coatings.

A preliminary appraisal of the coating and preparation of uranium and thorium carbide powders has been issued.[23] Some rate data are included for the deposition of carbon films for methane and acetylene in fluidized beds of alumina, uranium dioxide, uranium monocarbide, uranium dicarbide, and a solid solution of uranium-thorium dicarbide powders. Approximate conditions for the codeposition of uranium and carbon have been determined for a fluid-bed vapor-deposition process.

Production of Uranium Metal

Electrolytic Reduction of Uranium Dioxide

Sound uranium metal can be made from uranium dioxide by fused-salt electrolysis in cells using a consumable anode containing a uranium dioxide–carbon mixture. The cells are operated at temperatures above the melting point of uranium so that molten metal is formed. The cell consists of a cylindrical graphite crucible that serves both as the cathode of the cell and as a container for the molten electrolyte and molten metal. Several electrolytes have been evaluated at Weldon Spring,[24,25] and a composition corresponding to 65 per cent barium fluoride–10 per cent lithium fluoride–25 per cent uranium tetrafluoride gave the highest reduction rate and current efficiency of those tested. Other factors such as volatility, melting point, and cost will have to be considered before an optimum composition can be selected. Details of the reduction process were described in the October 1960 issue of *Reactor Fuel Processing*.[1]

Anodes are prepared by mixing uranium dioxide with coal tar pitch, pressing into shape, and carbonizing the pitch. The use of trichloroethylene as a solvent for the pitch has been found unnecessary. Two types of anode configurations have been evaluated: a "basket anode," which is a perforated graphite container holding chunks of the uranium dioxide–carbon mixture, and a "bare anode," which is a cylinder of the anode mixture immersed in the electrolyte. Preliminary tests[24] with the basket anode indicated that the graphite basket experienced considerable erosion by the formation of carbon tetrafluoride. As much as 18 per cent carbon tetrafluoride was observed in the off-gas. Carbon tetrafluoride is formed by the reaction of the graphite basket with uranium tetrafluoride in the fused salt, which lowers the uranium tetrafluoride concentration in the electrolyte such that periodic addition of green salt to the cell becomes necessary. Operation of the basket anode at 11 volts virtually eliminates production of carbon tetrafluoride through the formation of a nonconducting film over the anode surface. Supplying the cell current to graphite rods inside the basket also eliminates erosion by fluoride and oxide attack on the basket.

The use of the bare-anode cell design[25] offers the advantages of avoiding erosion of the graphite basket and depletion of uranium tetrafluoride from the electrolyte due to carbon tetrafluoride formation. Reduction rates with this anode are low (0.5 g of uranium per minute at 19 per cent current efficiency) compared to a basket anode in the same cell size (4.6 g of uranium per minute). Uranium recovery as massive metal, based on the weight of metal produced over the amount of uranium introduced as uranium dioxide and as uranium tetrafluoride, has exceeded 99 per cent.

Bomb Reduction of Uranium Tetrafluoride

Massive uranium metal is currently being produced at several AEC sites by a thermite reaction between uranium tetrafluoride and magnesium. The reaction is carried out in a closed steel bomb that is lined with recycled magnesium fluoride slag. Preignition heating of the charge is necessary to ensure liquation of

the reaction products and good slag metal separation; the heat of reaction at low temperature (< 150°C) is insufficient for this purpose. Ignition of the bomb after preheat is accomplished by electrically energizing a Nichrome coil located at the bottom of the bomb charge. Spontaneous ignition of bombs prior to scheduled electrical ignition results in higher metal costs since (1) metal yields are lower; (2) the resulting metal contains high hydrogen concentrations which must be removed either by vacuum outgassing or by recasting the metal; and (3) plant operation is more difficult to schedule.

Leifield and Weidman[26] in work done at Weldon Spring have investigated methods for controlling the heating period of the blended charges prior to spontaneous ignition. It was found that the factors which influence the spontaneous ignition of magnesium thermite bomb reactors are those which either directly or indirectly alter the rate of magnesium evaporation within the charge. Experimental evidence indicates that the bomb-reduction reaction probably initiates via the reaction between solid uranium tetrafluoride and gaseous magnesium. Preignition heating periods were lengthened by decreasing the furnace temperature, decreasing the surface area of the magnesium, filming the magnesium with magnesium oxide or magnesium fluoride, or by removing free uranium and magnesium from the bomb liner. Techniques that shortened preignition heating times included increasing the furnace temperature of magnesium surface area, decreasing the uranyl fluoride concentration in the green salt, adding to the bomb charge or liner substances that scavenge water and hydrogen fluoride, or removing water and hydrogen fluoride from the charge by purging with helium.

At the Feed Materials Production Center (Fernald, Ohio), the furnace used in the reduction of green salt to uranium metal is heated by circumferential resistance elements that tend to produce temperature gradients on the surface of the steel reaction vessel. The effect of these temperature gradients on crude derby yield, preheat time, and slag-metal separation was evaluated.[27] The furnace power input to the top and bottom elements of the reduction vessel was controlled so that the temperature gradient on the reduction-vessel surface was ± 56°C. In tests made with green salt containing 95.54 to 97.73 wt.% uranium tetrafluoride, there were no significant differences in average crude yields and average preheat time for the furnace power conditions used. When green salt containing 92.81 per cent uranium tetrafluoride was used under the same conditions, the preheat times were significantly longer but the crude yields were the same. In all cases the differences in power input to the heating elements and the resulting reduction-vessel surface temperatures were found to effect a variation in derby physical characteristics. A uranium plate was formed above the derby when higher temperatures were imposed on the upper surface. When opposite temperature conditions existed, uranium droplets interspersed in slag were found in the lower half of the derby.

A semicontinuous process for producing uranium by the reduction of green salt with magnesium in an induction-heated furnace is being investigated[28] in pilot-plant equipment. The charge material of green salt blended with magnesium is briquetted on a rotary press. The briquettes are fed from a belt conveyor through a two-door charging valve and into the heated reactor. The molten products of the reduction are separated by tilt-pouring into respective graphite molds. A 55-hr reduction-casting test was performed in a graphite reactor using enriched (0.94 per cent U^{235}) green salt. A charge rate of 30 lb of briquettes per minute was employed. After each reduction the major portion of the slag was poured from the reactor. After three reductions were made and the slag was removed, the uranium was cast into a graphite mold. The average crude derby yield was 95.9 per cent.

Recycled magnesium fluoride slag is presently used to line reduction vessels in the production of uranium metal. A new liner is fabricated for each reduction, and consequently there are, among liners, considerable differences in thickness, density, and chemical composition which produce variations in the yield and quality of the uranium metal product. A variety of refractories have been evaluated[29] as possible container materials to replace the magnesium fluoride liner. Of all materials investigated, magnesium oxide–aluminum oxide spinel was considerably more resistant to attack by the components of the uranium reduction system. The use of magnesium aluminate spinel as a crucible has been evaluated in the semicontinuous reactor.[30] Uranium metal made in the spinel reactor contained less carbon but more aluminum than that produced in a graphite-

lined reactor. Other impurity levels were similar.

An evaluation has been made on a small scale of a reusable graphite liner as a replacement for magnesium fluoride. Encouraging results[31] were obtained with a one-piece graphite liner fitted inside the steel bomb that had an annulus between the liner and the wall filled with powdered magnesium fluoride slag. As many as 28 reductions with a single liner were contained without failure. An extruded grade CS graphite proved superior to a high-density molded variety of graphite. Carbon content of uranium derbies averaged 22 ppm. A reusable graphite liner having consistent quality, dimensions, and properties would definitely tend to improve metal yields and quality. The elimination of the jolting operation used in packing the magnesium fluoride liner would reduce operating manpower and equipment. A pilot-plant evaluation of the graphite liner is planned to establish liner life and optimum processing conditions.

Direct Reduction of Uranium Hexafluoride to Metal

In the production of enriched uranium metal, uranium hexafluoride must be considered as the primary process feed material. Presently uranium hexafluoride is reduced to uranium tetrafluoride in an efficient, continuous process by hydrogen. The uranium tetrafluoride product is reduced to metal by either calcium or magnesium in a batch operation. Whereas the magnesium reduction of large quantities of unenriched uranium tetrafluoride incurs a low operating cost and is reasonably efficient, reduction of small batches of enriched uranium tetrafluoride is relatively inefficient and costly. The major items in the cost are the price of calcium, the difficulty of separating small amounts of uranium from the insoluble slag, and the increased handling imposed by small batch operations. Also, uranium recovery of greater than 99.9 per cent is required in processing highly enriched uranium. Two processes (high-temperature reduction with sodium vapor,[32] and reduction with sodium or lithium amalgam[33]) have been studied at ORNL to produce uranium metal by a one-step reduction of uranium hexafluoride. Although the engineering feasibility of these processes has not been demonstrated, nevertheless these processes have potential advantages of continuous operation with a primary uranium feed material, lower reagent costs, and lower operating and capital costs.

In the direct reduction of uranium hexafluoride to metal with sodium,[32] uranium hexafluoride and sodium vapor are continuously metered at atmospheric pressure into a reactor where they react according to the equation $UF_6 + 6Na \rightarrow 6NaF + U$. Details of preliminary development work were reported in a previous Review.[34] Process conditions were established in a reactor (Fig. V-1) composed of a 6-in.-diameter

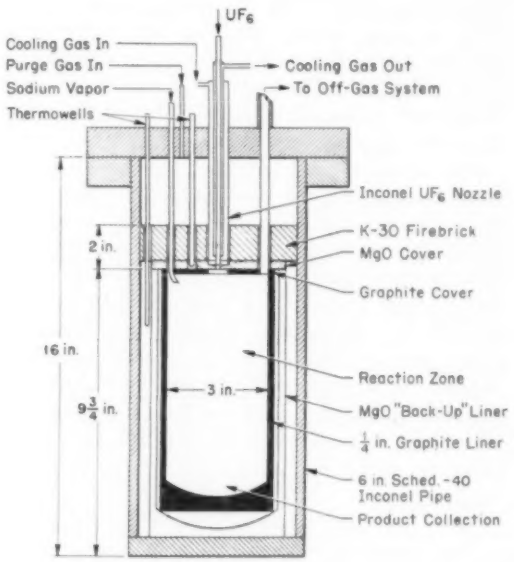

Fig. V-1 Schematic diagram of assembled reactor for direct reduction of uranium hexafluoride with sodium vapor.[32]

Inconel shell surrounding an insulated and graphite-lined reaction zone. The temperature of the reactor is maintained at 1200°C to produce a consolidated molten metal product and to ensure separation of the sodium fluoride slag.

It was observed that the reduction reaction proceeded rapidly and that significant reaction occurred at or near the tip of the uranium hexafluoride nozzle. This tended to produce high temperatures at the nozzle tip which necessitated heat removal at that point to prevent melting and excessive corrosion of the nozzle. Several nozzle designs were tested,

and in the final design the uranium hexafluoride inlet tube was surrounded by an Inconel jacket cooled by circulating gases. This nozzle was operated for short periods up to 44 min at reaction temperatures of 1200°C without significant damage.

Sodium excesses greater than 100 per cent, but not exceeding 200 per cent, appeared necessary for complete reduction. Relatively low uranium hexafluoride rates were necessary to ensure good mixing of the reactants. At best, 93.5 per cent of the uranium introduced was recovered as consolidated uranium metal of acceptable purity with the major contaminants being carbon, nickel, and iron. The recovery of uranium from the sodium fluoride slag can be accomplished by dissolution of the slag in hot water and filtration of the solution to remove the uranium-bearing solids.

Operation of the reactor was not entirely satisfactory in any demonstration test. The most serious problem has been and continues to be the development of a suitable liner to contain the reaction products (molten uranium and sodium fluoride) at temperatures as high as 1200°C. Magnesia, alumina, and graphite were used as liner materials, but all corroded, eroded, or cracked under operating conditions. Similar corrosion problems have been encountered[35] in the development of a process for reducing uranium hexafluoride to metal with magnesium at 1200°C. Boron nitride appears to be the only suitable crucible material.[35]

The feasibility of a one-step reduction of uranium hexafluoride to metal with sodium or lithium amalgam has been studied in laboratory-scale tests involving 1 to 100 g of uranium.[33] Three process schemes have been evaluated: a concentrated lithium amalgam process with 2*M* to 3*M* lithium mercuride in mercury as the feed; a dilute lithium process with a feed containing 0.7*M* lithium mercuride in mercury; and a process based on the use of sodium amalgam as the reducing agent.

Uranium hexafluoride diluted with argon is intimately mixed with a slurry of lithium mercuride in mercury at 25°C. The primary reduction reaction is $UF_6 + 6LiHg_3 \rightarrow UHg_4 + 6LiF + 14Hg$. Approximately 86 per cent of the uranium hexafluoride is converted to UHg_4; the balance is only partially reduced to uranium tetrafluoride. The product amalgam is a slurry containing UHg_4, unreduced uranium tetrafluoride, and by-product lithium fluoride in lithium amalgam. Vacuum filtration retains the UHg_4, uranium tetrafluoride, lithium fluoride, and some mercury while passing spent lithium amalgam along with 100 ppm uranium. Uranium tetrafluoride and lithium fluoride are washed from the amalgam residue and recovered separately. The washed uranium amalgam is introduced into a combined retort and furnace where the mercury is removed by distillation at 400°C under 0.5 atm of argon in the upper section of the retort to produce a uranium sponge. As the charge moves vertically down the furnace, the sponge is melted and consolidated to massive metal at 1225°C. With the exception of mercury, the concentration of impurities present in the final uranium metal product was lower than for electrolytic-grade metal.

Both the concentrated and dilute lithium amalgam processes produced the same UHg_4 yield in demonstration runs. Preliminary results indicate that the maximum conversion to UHg_4 in the sodium amalgam process is limited to 40 per cent. Evidently the sodium reduction tends to terminate with the formation of uranium tetrafluoride or a uranium tetrafluoride–sodium fluoride complex, and further reduction is not possible below 350°C.

Recovery of Uranium from Magnesium Fluoride Slag

In the production of uranium metal by reaction of uranium tetrafluoride with magnesium, the large quantities of magnesium fluoride slag which are produced may contain up to 7 per cent uranium. Studies at the Oak Ridge Gaseous Diffusion Plant[36] have indicated that direct fluorination employing either fluid-bed or vibrating-tray reactors was a feasible means of recovering uranium from the slag. Uranium content of the magnesium fluoride was reduced to 0.4 per cent at 400°C in an atmosphere of 92 per cent fluorine. The powder time in the reactor was approximately 0.5 hr. Greater uranium recovery is expected by operating at a higher reactor temperature and by using a finely ground feed.

A process for the continuous digestion of magnesium fluoride slag to recover uranium has been successfully tested on a plant scale at the Metals Recovery Plant at Fernald, Ohio.[37] In this process a water slurry of slag is transferred at a fixed rate and concurrently reacted with hydrochloric acid. The reaction of

free metal with either water or hydrochloric acid results in the generation of hydrogen gas. To obviate any violent reactions resulting from ignition of hydrogen, the hydrogen concentration in the system is held below 1.0 vol.% by controlling both the acid and slurry feed rates. Uranium content of the discard tailings consistently analyzed less than 0.17 per cent uranium.

Production of Thorium Metal and Alloys

Raleigh has reported work on the preparation of thorium-aluminum alloys by the direct reduction of thorium oxide into an aluminum melt.[38] The optimum reductions were obtained with 25 wt.% thoria and 75 wt.% cryolite (Na_3AlF_6) as the initial salt phase. Under these conditions, 97 per cent reduction occurs in 0.5 hr at 1050°C. Nearly quantitative reduction yields were obtained in preparing alloys that contained up to at least 20 wt.% thorium, whereas alloys that contain up to 40 wt.% thorium can be prepared only with a significant loss in reduction yield.

The reaction rate is independent of the thoria particle size below 2 μ in diameter. The rate is apparently increased by inductive stirring of the metal phase. The predominant driving force for the reaction is the large free energy of formation of the intermetallic compound $ThAl_3$. Since uranium dioxide is also reducible from cryolite baths with aluminum, this concept may be easily extended to produce thorium-uranium-aluminum alloys of a wide range of composition.

An interesting side reaction was observed in all runs, where aluminum reacted with cryolite to produce gaseous sodium according to the reaction $Al + Na_3AlF_6 \rightarrow 3Na + 2AlF_3$. This sodium may be considered an economic by-product in the production of thorium-aluminum alloys, although means by which the sodium might be collected have not been explored.

Recently published are the results of preliminary work conducted by the U. S. Bureau of Mines, Albany, Oreg., on the production of thorium metal by reduction of thorium tetrachloride with sodium.[39] Most of the information presented has appeared in previous Reviews.[1,40] Development work is continuing[35] on both the preparation of purified thorium tetrachloride from thorium oxalate and reduction of purified chloride with sodium.

Plutonium Metal Preparation

Rasmussen and Hopkins[41] have published details on the preparation of plutonium metal from plutonium trichloride. This work, performed at Hanford, was reviewed previously.[14] In this study[41] plutonium trichloride was prepared by reaction between plutonium dioxide and phosgene at 500°C. An average plutonium trichloride yield of 98 per cent was consistently obtained. Results of the chlorination of plutonium dioxide, Pu(III) "carbonate," and Pu(III) and (IV) oxalates by either phosgene or hydrogen chloride have been published,[42,43] and a method of synthesizing plutonyl chloride ($PuO_2Cl_2 \cdot 6H_2O$) has been described.[44]

A series of investigations was carried out at ANL[45] to evaluate the possibility of preparing plutonium metal by electrolysis from the double chloride salt of cesium and plutonium (Cs_2PuCl_6). Attempts to obtain plutonium from solutions of Cs_2PuCl_6 in cesium chloride by electrolysis at 700°C were unsuccessful. The cells employed graphite anodes and molten plutonium cathodes. More encouraging results were obtained using the double chloride salt as an electrolyte for electrorefining impure plutonium metal. A 14 wt.% solution of Cs_2PuCl_6 in a potassium chloride–lithium chloride eutectic was electrolyzed at 550°C using tantalum cathodes and impure plutonium anodes. In a preliminary test a 70 per cent efficiency was observed by operating at 0.6 volt and 1.5 amp. Work with this cell is being continued.

The complete proceedings of the Grenoble, France, International Conference on the Metallurgy of Plutonium, described in a previous Review,[14] have been published.[46] These volumes represent an excellent source of material on the physical metallurgy of plutonium metal and alloys.

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